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References:

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Sahni, B. (1936a) Wegener's theory of continental drift in the light of Palaeobotanical evidence. *J. Indian bot. Soc.*, **15**: 31-32.

Sahni, B. (1936b) The Karewas of Kashmir. *Curr. Sci.*, **5**: 10-16.

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Bionomics of *Ptychodera flava* Eschscholtz * (Enteropneusta)

BY

K. Pampapathi Rao [1]

University Zoology Laboratory, Madras

(Received December 30, 1953)

ABSTRACT

Ptychodera flava occurs in three types of localities in the Krusadai and adjacent islands in the Gulf of Mannar, namely, in the coral sand, rough coral detritus exposed to strong surf and in the crevices of dead corals where there is no sand. Burrowing is accomplished by co-ordinated muscular and ciliary activity, while locomotion on hard surface is mainly aided by ciliary activity. On occasions ingestion of free solid organic matter has been observed. Excepting the branchial basket, the whole surface of the body exhibits phosphorescence and this perhaps is due to some substance present in the surface mucus. Sexes are dimorphic and a hyperpolygamous sex-ratio of one male to 65 females has been observed. The spawn is driven out of the burrow by strong and repeated peristaltic waves passing over the body from behind anteriorwards. From the occurrence of tornaria belonging to this species during different seasons of the year more than one breeding periods annually are postulated.

Since Willey's (1899) notes on the biology and morphology of *Ptychodera flava,* few observations have been made regarding the habits and habitat of these forms and these are summarized in Horst (1927-'39) and Dawydoff (1948). As part of a detailed study of the bionomics, anatomy, early development and regeneration of *P. flava,* the following observations were made in the field and on live material brought to the laboratory.

Ptychodera flava occurs in three different types of habitats in the Krusadai and adjacent islands in the Gulf of Mannar. The so-called 'Balanoglossus area' on the southern shore of the island, is a flat shallow area of the lagoon bed, lying between tide marks, from where, during low tide, an average of six specimens may be collected from every cubic foot of sand. *Edwardsia* and sand-dwel-

* Part of thesis approved for the Ph.D. degree of the Madras University.

1. Present address: Department of Zoology, Andhra University, Waltair.

ling copepods (*Paramesochra arenicola, P. wilsoni* and *Emertonia minuta*) constitute the animal community. On the southern shore of the Shingle island, *P. flava shinglensis* inhabits the rough coral detritus which is exposed to the action of breakers. This area is very restricted and no other animals are found in this habitat. On the northern side of the Shingle island, however, *P. flava coralliformia* occurs in the rocky beach between tide marks. It inhabits crevices in the dead coral rocks, where there is no sandy element and the coral rocks are tenanted only by forms like *Lithodomus*, lobsters and sea-anemones.

Most of the following observations were made at the Krusadai Biological Station on material collected from the first named locality.

While the area is covered by water at high tide, the organisms were seen with the anterior half of their bodies on the surface of the sand. The posterior half was buried within the sand to a depth of two to three inches. It appeared that there was no distinct burrow while the animal is covered over with water at high tide. But the situation was entirely different at low tide, when the area was exposed. Each individual was confined to a U-shaped burrow typical to most enteropneusts.

Burrowing is accomplished by a co-ordinated muscular action greatly aided by the activity of the proboscis and collar ciliature. As soon as the elongated tip of the proboscis comes in contact with the surface of the sand, a layer of sand particles could be seen streaming posteriorly over the surface of the proboscis and thence backwards over the collar. Thus, due to strong ciliary action, the surface of the sand in contact with the tip of the proboscis is actualy hollowed out. Into this depression in the sand the narrowed tip of the proboscis penetrates. The anterior part of the proboscis which has entered the sand now swells up. The tip of the anterior swollen region of the proboscis further penetrates into the sand, where again it dilates, and thus the process is repeated. The penetration and the subsequent swelling up of the anterior part of the proboscis provided the grip, drawing the posterior regions of the body in the wake of the proboscis.

Movement on level surface is mainly aided by the action of the epidermal cilia supplemented to a great extent by the peristaltic waves, which arise at the tip of the proboscis and travel backwards.

Such seems to be the mechanism of locomotion in *P. flava coralliformia,* which occurs in crevices of dead coral rock, where there is no sand substratum to burrow in. I have observed on more than six or seven occasions individuals penetrating and forcing their way through bits of other individuals found in their vicinity in the aquaria. In a few cases such bits have been seen to pass over the whole length of the entire animal, helped by the peristaltic movements of the body as well as by the action of the cilia.

Although like all other enteropneusts *P. flava* feeds on organic matter contained in the sand taken in while burrowing and in water taken in by ciliary activity (Barrington, 1940), an interesting case of ingestion of free solid organic matter was observed in the aquaria. Larger specimens were observed in the process of ingesting small broken bits which were lying free in the acquaria. Since there was no sand substratum, the larger ones might have just run over the small bits, which must have been caught up in the space between the proboscis and the anterior funnel of the collar and thence driven into the wide-open mouth by the strong ciliary action of the pre-oral ciliary organ. This capacity for ingestion of small freely occurring food material probably explains how forms such as *P. flava coralliformia* feed in the crevices of dead corals and on rock surfaces where little or no sand is found.

All parts of the body, excepting the branchial basket, produce a bright greenish light on slight irritation. Even such a slight irritation, like their movement on the rough sandy substratum caused light production and a trail of greenish glow could be seen indicating the location of the organism. Light has an inhibitory effect on the phosphorescence of these animals. Exposure to light even for a short while greatly inhibits subsequent phosphorescence. Isolated fragments reacted in the same way as entire animals. When the water in the container was stirred, bright greenish streaks of phosphorescent mucus could be seen flashing along the current. Hence it appears that the phosphorescence is due to some substance contained in the mucus secreted by the animal.

Sexes are dimorphic, the males being readily identifiable by the presence of flecks of dark brown pigment patches on the genital pleurae. Males are hard to come by because of the hyperpolygamous sex-ratio of one male to about 65 females. This is the only known enteropneust with such a high percentage of females.

The first indication of spawning is the exudation of a milky substance from the burrow, while the proboscis and collar of the animal could be seen at the mouth of the burrow moving up and down. Strong and repeated peristaltic waves pass over the body, which probably drive the genital products towards the mouth of the burrow. From here movements of the proboscis and the collar scatter the eggs or sperm. In the still waters of the aquaria, however, some of these eggs could be seen forming clumps. It is possible that in *Balanoglossus calvigerus* the grouping together of eggs which Heider (1909) described may be due to the lack of disturbance in the aquaria as suggested by Horst (1927-'39), and that in the natural condition eggs are scattered as Stiasny (1914) observed. However, Dawydoff (1948) and Burdon-Jones (1951) have observed a massing of eggs in *Glossobalanus minutus* and *Saccoglossus horsti* respectively. Spawning in males of *P. flava* closely resembles that in females and the sperm is discharged as a thick cloud of whitish milky substance.

Devanesan and Varadarajan (1940) concluded, after a cursory examination of the state of maturity of the gonads, that in *P. flava* the breeding season occurs somewhere about the period extending from December to February. However, spawning by individuals in aquaria was observed by me in August and March, but this may be due to the shock of collection. In any case the percentage of mature individuals was considerably high during March. Burdon-Jones (1951) concluded that there is a breeding season for the different enteropneusts. It is probable that two or more breeding periods occur in a year, since swarms of tornaria at the same stage of development and belonging to the same species were obtained in plankton collections by me (Pampapathi Rao, 1953; 1954) as well as by earlier workers, more than once during the year.

ACKNOWLEDGEMENT

I express my sincere thanks to Prof. C. P. Gnanamuthu, Director, University Zoology Laboratory, Madras, under whose encouraging guidance the present investigation was carried out. To the Asst. Director of Fisheries, Madras Government, I am thankful for all the laboratory and collection facilities given me at the Krusadai Biological Station in the Gulf of Mannar. Mr. S. Krishnaswamy of the University Zoology Laboratory, has kindly identified for me the sand-dwelling copepods listed in this paper.

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Commentaria Herbarii:

"Presidency College, Madras-5"

2. On the floral biology of some members of the Anonaceae

BY

K. Periasamy

Department of Botany, Presidency College, Madras-5

(Received January 19, 1954)

ABSTRACT

Observations on the mechanism of anther dehiscence in *Polyalthia longifolia* Hook. f. & Thoms. and the method of pollination in *Cananga* Hook. f. have been recorded.

The anthers of *Polyalthia longifolia* exhibit a successive "catapulting" movement of the walls of the anther cells, and this mechanism repeats itself two or three times. At the end of each "catapulting" the stamen as a whole is subjected to violent tossing. The final result is that all the pollen grains contained in the anther become effectively dispersed.

In *Cananga odorata*, the androecium as a whole becomes separated from the thalamus, dragging with it the stigmatic heads. Thus, not only self pollination is prevented, but the chances of cross pollination (which, however, becomes the rule) is also minimised. This phenomenon accounts for the low percentage of fruitset in this species.

Literature pertaining to the mechanism of anther dehiscence appears to be rather meagre. Although some accounts have been published in regard to the histology of the anther wall during ontogeny, there have been very few authentic records of actual observations on the method of dehiscence under natural conditions.

In connection with certain morphological studies on the Anonaceous representatives that are being at present pursued in this Laboratory, some rather peculiar methods of dispersal of mature pollen grains were encountered which form the topic of this contribution.

1. *Polyalthia longifolia:*

Before maturity of the essential organs of the flower, the perianth members are widely open exposing to view the compact androecium and gynoecium (Fig. 1). The stigmatic heads project

above the surface of the androecial members which are characterised by the possession of flat-hooded prolongations of the connectives. * Thus, due to the close crowding of the androecial members and the hood-shaped prolongations of the connectives, the anther thecae become concealed when seen from above. The position of the thecae on the connective is more towards the abaxial side of the sporophyll. The apices of the thecae are fused with the under-surface of the hood (Figs. 3, 4, and 5).

At maturity, the stigmatic surface becomes glistening indicating its receptiveness. The androecium also changes its colour from white to light brown. The bases of the three inner perianth members converge over the essential organs so as to completely mask them from view, excepting for a small opening in the centre just above the stigmatic surface (Fig. 2).

The anthers begin to dehisce between 10 to 12 A.M., and two hours later all the individual anthers become separated from the thalamus and lie loose inside the chamber formed by the bases of the inner perianth lobes.

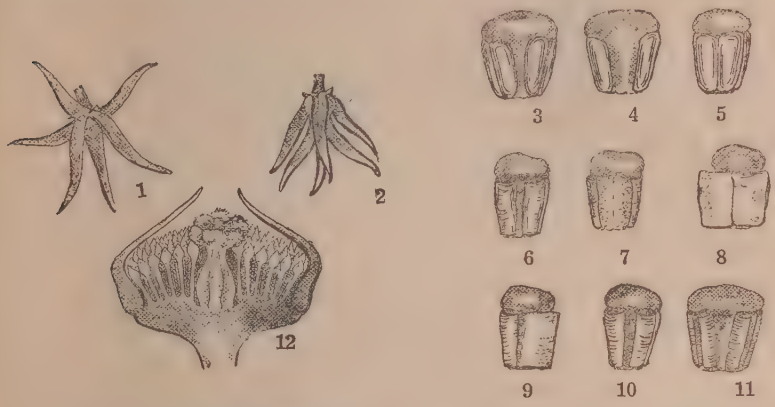
The mature anthers, when removed from the flower and placed on a slide, begin to dehisce within half to one minute. The wall of each cell of the anther splits longitudinally along the line of contact of the two thecae (Fig. 6). Then they begin to open out and diverge steadily in the form of membranous flaps, exposing to view the pollen grains lodged inside the anther cell (Fig. 7). As the anther walls so open out, their terminal attachment with the connective also gets severed.

The splitting and gradual opening out (which can be seen even with the naked eye) continues for half to one minute and at the end of this period the flaps are completely open, so that they appear as completely flattened structures. As a result, the entire interior of the anther cell is now presented to view and the pollen grains are found adhering throughout the surface (Fig. 8).

Now, suddenly, one sees the flat flap belonging to one of the thecae, swinging back to its original position (the position in the undehisced anther), while the flap of the other theca of the same cell remains open (Fig. 9). The swinging movement of the flap is

* Recent investigations appear to emphasize the advisibility of employing the non-commital term "microsporophyll" for the so-called stamens of the Ranalian families (Swamy and Bailey, 1949), instead of designating the structures through controversial terms like "anther", "filament", "connective", etc. However, for the sake of simplicity the term "connective" is employed here in a purely descriptive sense without any implications of phylogeny.

so rapid and violent that the entire anther lying on the slide is jerked and thrown off a few centimeters.



Figs. 1-11. *Polyalthia longifolia.* Fig. 1. Flower before the maturity of the essential organs. Fig. 2. Same, at the time of anther dehiscence. Fig. 3. Stamen, abaxial view. Fig. 4. Adaxial view. Fig. 5. Lateral view. Fig. 6. Same, soon after the splitting of the anther cell. Fig. 7. Same, when both the thecae walls of a cell are in the process of opening out. Fig. 8. Flaps fully open. Fig. 9. One of the flaps swung back. Fig. 10. Both flaps swung back. Fig. 11. Abaxial view of the stamen after both the cells become empty and the flaps re-assume the original position.

Fig. 12. Sagittal longitudinal section of a flower of *Cananga odorata;* outer perianth not shown. For further explanation see text.

While the swung back flap of this theca thus remains closed, the flap belonging to the other theca—which until now remains open, Fig. 9—soon follows the same sequence of events as exhibited by its counterpart; as a result, the anther is again thrown off in another direction.

The concomitant result of the "catapulting" of the two thecae walls *one after the other* appears to result in an advantage. Thus, the pollen grains that adhere to one flap and then those sticking to the other flap are scattered at successive intervals. If, on the other hand, the "catapulting" of the two flaps of an anther cell were simultaneous, most, if not all, of the pollen grains of the cell would have fallen again into the same anther cell.

Not only this. The closing in of the flap is so violent that the entire pollen grain mass adhering to the inner face (the side adjoining the connective) of the anther cell also become loosened, and some of the loosened pollen grains now stick to the inner surface of the flap. When this phenomenon has been accomplished

in both the cells of an anther, the entire stamen re-assumes its original shape, resembling that before dehiscence. Now, however, each anther cell is split longitudinally (Figs. 10, 11).

Now the flaps with the pollen grains adhering to the inner surface again open out and diverge. The same sequence of events described for the first dehiscence repeats itself. Only, the time taken for the entire opening and closing is considerably less. The same story is repeated *in toto* three or four times towards the end of which almost all the pollen grains of the anther cell escape out of their cavities.

It must be noted that in the flower the entire dehiscence takes place inside the chamber formed by the converging lower portion of the inner perianth members. It is obvious that the violent movements of the flaps of the two cells of an anther exerts spacial influences on its neighbouring androecial members due to their compact arrangement. Thus, due to the mutual influences of the individual members of the androecium the stamens become separated off the thalamus and come to lie loose inside the perianthial chamber. The pollen grains that are disseminated from the thecae also become scattered in this chamber. The only method of escape for these pollen grains is through the narrow aperture at the apex of the perianthial chamber, or through the very narrow slit-like space between the adjacent margins of the bases of the inner perianth members in the region of the perianthial chamber. However, there is no way for the pollen grains to really escape out of imprisonment until the perianth members drop off in the usual way, setting free the pollen as well as the dehisced stamens to environment. And this phenomenon takes place only 24 hours after the dehiscence of the stamens.

2. *Cananga odorata*

This plant is interesting in exhibiting another method which has nothing to do with the individual stamens, but concerns the entire androecium.

Even though this plant produces an abundant number of flowers almost throughout the year, comparatively very few fruits develop. An examination has revealed that there has been a considerable degree of sterility which results through the degeneration at every step in the development of the female gametophyte. But this alone is not adequate to explain the abnormally low percentage of fruit-setting. However, the behaviour of the androecium as a whole appears to offer a cogent explanation.

The androecium is compactly packed on the convex thalamus whose centre is occupied by the gynoecium. This entire set-up is in turn pressed on all sides by the basal portions of the inner perianth members. The apocarpous gynoecium is also closely crowded and collectively appear in the form of a broad-hooded cone with a narrow neck (Fig. 12). The basal portion represents the ovule-bearing part, the short narrow middle portion the stylar part, and the broad-hooded portion the stigmatic part. The stigmatic part projects and expands immediately beyond the androecium. The stylar part is in line with the level formed by the pointed prolonged connectives of the stamens. The pointed tips of the connectives immediately surrounding the gynoecium are deeply embedded in the tissues of the stigmatic head.

The flower droops down at maturity and the stigmatic head appears glistening indicating its ready receptiveness. At this time the apical surface of the androecium is of a brownish white colour.

After a lapse of 36 to 72 hours, the colour of the androecium becomes dark brown, thereby indicating that the anthers are attaining the stage of dehiscence. After dehiscence, the pollen grains that are liberated are entrapped in the narrow spaces between the pillar-like columns of the stamens which are enclosed by the basal parts of the inner perianth members, and also on the floor of the thalamus.

This phenomenon appears to be accomplished between 12 A.M. and 1 P.M., subsequent to which the inner perianth members wither and drop off around 3 P.M.

The field-observation of the foregoing events convinces one that the androecium as a whole was kept in tact even during the anther dehiscence only on account of the pressure exerted on the androecium by the inner perianth members. Soon after the dropping off of the perianth, the stamens in a body shoot off from the thalamus *carrying with them* the *collective stigmatic head.*

Now, nothing can be seen of the androecium which existed a minute ago in the flower, nor of the pollen grains that were entrapped amidst the androecial members. By this method it is obvious that the pollen grains have failed to reach the stigma of the same flower. Thus, the "de-capitated" gynoecium alone is left *in situ* on the thalamus.

The chances of self pollination thus being ruled out, the flower becomes adapted to cross pollination alone. Even this is circumscribed by other factors, the end result being the low percentage of fruit-set.

One of the major factors standing in the way of generous and successful cross pollination is the separation of the stigmatic head early in ontogeny. When this takes place, the pollen of the same flower (although is liberated from the anther cells) does not become accessible for the stigma. At the same time, it must be remembered that if fruit-set is to be accomplished,

(a) the pollen liberated from a neighbouring flower should find its way on to the stigma,

(b) these pollen grains should germinate, and

(c) should produce pollen tubes long enough to reach the ovule-bearing part of the carpel, i.e., the level below the "decapitation" point of the gynoecium. Such severed ends of gynoecia proved to be an unfavourable substratum for the reception and germination of pollen grains.

All these steps should be accomplished before the stigmatic head becomes severed off. Thus these factors work as a limiting influence upon free fruit-set. In addition to these, the failure of any kind of insects visiting the flowers and the absence of contrivances for anemophily play a corollary role in still further reducing the percentage of fruit-set.

Conclusion

This preliminary study suggests the possibility of encountering diverse methods of anther dehiscence and pollination among the members of the family. Furthermore, both the genera studied here belong to the same tribe Unoneae. Thus, it is to be hoped that further observations of similar nature may yield valuable clues in regard to the internal taxonomic segregations and their mutual inter-relationships within the family.

Acknowledgement

I take this opportunity to express my appreciation to Dr. B. G. L. Swamy, Chief Professor of Botany, Presidency College, without whose guidance and assistance this note would not have been written.

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Role of Carbohydrates on the Biosynthesis of Nicotinic Acid in Germinating Green Gram

(*Phaseolus mungo*)

BY

E. R. B. Shanmuga Sundaram and P. S. Sarma

(*University Biochemical Research Laboratory, Guindy Madras-25*)

(Received February 1, 1954)

ABSTRACT

A study on the effect of various carbohydrates like glucose, fructose, sucrose, mannose and half glucose half fructose mixture on the biosynthesis of nicotinic acid when present in the medium during germination of green gram has been made. It is found that whereas the presence of glucose or mannose has no influence on the biosynthesis of nicotinic acid, the presence of fructose and sucrose lowers the nicotinic acid synthesis. As the seeds are germinated in a sterile condition, the adverse effect produced by fructose or sucrose is attributed to the hitherto unknown metabolic role of the carbohydrates in the conversion of tryptophan to nicotinic acid.

A modified form of the chemical method of nicotinic acid has been worked out. The method is found to give values agreeing very well with that obtained by the microbiological assay.

The consumption of maize was associated with pellagra by a number of early workers (Goldberger, Wheeler, Lillie & Rogers, 1929, Handler, 1943). In their studies on the growth depression produced by maize, Krehl, Teply, Sarma and Elvehjem, (1945) observed that the kind of carbohydrate in the diet modified the effect of maize. When glucose was the carbohydrate in the diet the adverse effect of maize on the growth of rats was diminished compared to that with sucrose as the carbohydrate. The Wisconsin group of workers (Mannering, Orsini and Elvehjem, 1944; Schweigert, McIntire, Henderson and Elvehjem, 1945) showed that the type of carbohydrate used in the diet had a marked influence on the synthesis of vitamins in the intestinal tract. They further showed that glucose, dextrin and to a lesser degree lactose exerted a marked influence in modifying the undesirable effect of maize, whereas sucrose enhanced the adverse effect. From these observations it was concluded that maize produced alterations in the

intestinal flora, and that the type of carbohydrate used was important in determining the extent of these changes. The growth inhibition was overcome by the administration of nicotinic acid or tryptophan.

Whether the influence of carbohydrates in overcoming the adverse effect of maize was a specific case or the same phenomena was exhibited in the case of other tryptophan low proteins similar to corn was tested by Krehl, Sarma, Teply and Elvehjem (1945). Diets containing wheat gluten and gelatin were tested using sucrose, dextrin, glucose and corn starch as the carbohydrate component. Only in the case of sucrose rats showed growth inhibition followed by growth stimulation after the addition of nicotinic acid, or tryptophan as in the case of corn diet. Thus they established that carbohydrates had a role in the conversion of tryptophan to nicotinic acid. The efficiency of carbohydrates in counteracting nicotinic acid deficiency in the rat decreased in the following order: dextrin, glucose, corn starch and sucrose. The role of carbohydrates was attributed to their ability to the establishment of an intestinal flora capable of synthesising adequate amount of the deficiency factor.

Recent work of Hundley (1949) pointed out the possibility that varying amounts of nicotinic acid might be required in the metabolism of different carbohydrates. Using a synthetic diet with 9 percent casein and various carbohydrates like fructose, sucrose, half glucose-half fructose mixture, glucose, starch and maltose, he found that starch, glucose and dextrin gave relatively good growth, but more nicotinic acid was actually required in the case of fructose, sucrose and half glucose-half fructose mixture. He attributed a metabolic role for the carbohydrates in the conversion of tryptophan to nicotinic acid. In the present investigation sterile germinating seeds were used as the organism to eliminate micro-organisms and the influence of carbohydrates like glucose, fructose, sucrose, half glucose-half fructose mixture and mannose was found out during germination of green gram.

EXPERIMENTAL

Germination of seeds: 5 gm. lots of green gram were freed from bacterial and fungal contamination by treating with 0·1 percent mercuric chloride solution and immediately washing off the seeds by thoroughly shaking with sterilised distilled water a number of times. The seeds were transferred asceptically into dry sterile

petri dishes. Sterile glass distilled water (25 cc) was added to one petri dish (control) and varying amount of a sterilised solution of the various carbohydrates along with sterile glass distilled water (to make up the volume to 25 cc) were added to some dishes. The germination was allowed to take place in sterile chambers that had been protected against direct sunlight. They were harvested at the end of the germination period and analysed for the total nicotinic acid.

Estimation of nicotinic acid plus nicotinamide in dry and germinated seeds

Principle: The pyridine nucleus in the nicotinic acid is broken up by cyanogen bromide (Konig reaction) and the residue with aniline gives a yellow pigment, the intensity of the yellow colour of the pigment being directly proportional to the amount of nicotinic acid.

Procedure: The germinated seeds were ground well with about 30 cc. of water and hydrolysed with 10 cc. of 12N sulphuric acid over a boiling water bath for 45 minutes, centrifuged after cooling and the supernatant made up to 50 cc. washing the residue twice or thrice. 25 cc. of the solution was pipetted out into a conical flask, 5 cc. of 60 percent basic lead acetate solution added, shaken well and the pH adjusted to 9·4 with 40 percent sodium hydroxide using thymol blue as external indicator.

The product was then centrifuged, the supernatant solution taken for further work and the residue was discarded. By this process most of the proteins and to some extent the colouring matter were removed. The supernatant liquid was then treated with 2 cc. concentrated sulphuric acid (36N) to remove excess of lead acetate and allowed to stand for an hour and finally centrifuged. The supernatant liquid was treated with 5 cc. of 40 percent zinc sulphate solution and the pH brought to 8·4 with 10N sodium hydroxide, using phenolphthalein as external indicator (appearance of a slight pink colour). The product was then centrifuged. By the above process all the proteins and most of the colouring matter were removed. The solution was brought to pH 7·0 with 6N hydrochloric acid using bromo thymol blue as external indicator and the volume of the solution obtained was noted. To avoid unnecessary dilution washings must be done wherever necessary with minimum amount of water.

Colorimetric analysis:

Colorimetric analysis were made in a "Lumetron" photoelectric colorimeter according to the method of Hawk, Oser and Summerson (1947). Two centre settings were necessary, one for evaluating the residual colour in the test solution and the other for the colour developed in the reaction. The colorimeter was set at 100% transmittence with:

(i) 3 cc. water +7 cc. alcoholic buffer.

(ii) 3 cc. test solution + 7 cc. alcoholic buffer — (A)

The colorimeter was set at 100+ transmittence with reagent blank:

(i) 3 cc. water + 6 cc. cyanogen bromide + 1 cc. aniline in absolute alcohol.

(ii) 3 cc. test solution + 6 cc. cyanogen bromide + 1 cc. aniline in absolute alcohol — (B)

(iii) 3 cc. test solution + 6 cc. cyanogen bromide + 1 cc. aniline in absolute alcohol + 0·1 cc. standard nicotinic acid containing 10 gamma — (C)

Calculation: The galvonometer reading (G) was converted to photometric density (P.D.) by using the formula P.D. = 2—log G. The nicotinic acid was calculated using the formula

$$\frac{\text{B minus A}}{\text{1·01C minus B}} \times 10 \times \text{dilution factor} \times 2 = \text{amount of nicotinic acid in gamma present in the weighed amount of seeds taken (5 gm.)}$$

Note: The above method is a slightly modified form of the general chemical method of nicotinic acid estimation and is found to give values agreeing very well with that obtained by the microbiological method of Snell and Wright (1941).

Microbiological method:

In the microbiological assay the test organism used was a pure culture of *Lactobacillus arabinosus* (17-5) and the estimations were carried out according to the method of Snell and Wright (1941). The basal medium used had the following composition.

Acid hydrolysed casein	0·5	percent
L-tryptophan	0·01	"
L-cystine	0·02	"
D (+) glucose	2·0	"
Sodium acetate	2·0	"
Adenine, guanine & uracil (each)	10·0	p.p.m.
Thiamine, PABA, calciumpantothenate (each)	0·10	p.p.m.
Riboflavin & pyridoxin (each)	0·20	p.p.m.
Biotin	0·20	p.p.b.
Inorganic salts A & B (each)	0·5	ml.

Results and Discussion:

The results obtained for the biosynthesis of nicotinic acid when the seeds are germinated in presence of the various carbohydrates in solution with water are presented in Table I and the data in Table II gives the amount of nicotinic acid formed when the seeds are germinated in presence of different carbohydrates along with L-tryptophan. From Table I, it can be seen that the presence of glucose or mannose in the medium during germination has no effect on the biosynthesis of nicotinic acid, whereas the presence of fructose or sucrose or half glucose-half fructose mixture produces an inhibition in the synthesis of nicotinic acid. There is a definite increase in the synthesis of nicotinic acid when the seeds are germinated with L-tryptophan as is seen from Table II. Here again, in the medium containing tryptophan, the additional presence of glucose or mannose has no effect (inhibitory or enhancing) whereas the presence of fructose or sucrose exerts an inhibitory effect with consequent decrease in the biosynthesis of nicotinic acid. From these data, it is clear that fructose and sucrose are concerned in some manner in the biosynthesis of nicotinic acid from tryptophan. As the seeds are made sterile before germination and found free from bacterial contamination, the inhibitory nature of fructose or sucrose can be due to a metabolic role of these carbohydrates in the biosynthesis of nicotinic acid.

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TABLE I

Influence of various carbohydrates on the biosynthesis of nicotinic acid during germination of green gram in water medium.

(Initial nicotinic acid in dry seed = 20.8 gamma per gm.)

Figures are expressed in microgram per gram of dry tissue.

Substances in the medium	Period of germination	
	48 hours	72 hours
1. 30 cc. Water (Control)	30·2	38·6
2. 30 cc. Water containing 200 mg. glucose	31·3	40·1
3. 30 cc. Water containing 200 mg. fructose	24·6	28·2
4. 30 cc. Water containing 200 mg. sucrose	25·3	29·8
5. 30 cc. Water containing 200 mg. mannose	30·1	39·6
6. 15 cc. Water containing 100 mg. fructose plus 15 cc. water containing 100 m. sucrose.	25·8	30·4

TABLE II

Influence of various carbohydrates on the biosynthesis of nicotinic acid during germination of green gram in L-tryptophan medium.

(Initial nicotinic acid in dry seed = 20.8 gamma per gm.)

Figures are expressed in microgram per gram dry material.

Substances in the medium	Period of germination	
	48 hours	72 hours
1. 30 cc Water alone	30·8	39·2
2. 20 mg. L-tryptophan in 10 cc. water + 20 cc. water	41·0	46·8
3. 20 mg. L-tryptophan in 10 cc. water + 20 mg. glucose in 20 cc. water.	40·3	44·2
4. 20 mg. L-tryptophan in 10 cc. water + 200 mg. fructose in 20 cc. water	29·5	38·0
5. 20 mg. L-tryptophan in 10 cc. water + 200 mg. sucrose in 20 cc. water	31·6	39·8
6. 20 mg. L-tryptophan in 10 cc. water + 200 mg. mannose in 20 cc. water	39·4	43·6
7. 20 mg. L-tryptophan in 10 cc. water + 100 mg. fructose in 10 cc. water + 100 mg. sucrose in 10 cc. water.	30·5	38·6

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Studies on South Indian Fusaria. III. Fusaria Isolated From Some Crop Plants

BY

C. V. SUBRAMANIAN

University Botany Laboratory, Madras

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ABSTRACT

A systematic account is given of the Fusaria isolated from some crop plants from South India. The host plants and the various Fusaria which were isolated from them are listed below:

Amaranthus sp.

* Fusarium semitectum Berk. & Rav.

Ananas sativus Schult.

* Fusarium coeruleum (Lib.) Sacc.
* F. javanicum Koorders
* F. solani (Mart.) App. et Wr. v. striatum (Sherb.) Wr.

Cajanus cajan (Linn.) Millsp.

* Fusarium udum Butler

Cicer arietinum Linn.

* Fusarium orthoceras App. et Wr.
Fusarium solani (Mart.) App. et Wr. v. martii (App. et Wr.) Wr.
* F. solani (Mart.) App. et Wr. v. minus Wr.

Coriandrum sativum Linn.

* Fusarium chlamydosporum Wr. et Rg.
* F. avenaceum (Fr.) Sacc.
* F. equiseti (Corda) Sacc.
* F. solani (Mart.) App. et Wr. v. minus Wr.

Cyamopsis tetragonoloba Taub.

* Fusarium semitectum Berk. & Rav. v. majus Wr.
* F. scirpi Lamb. et Fautr.
* F. oxysporum Schlecht.
* F. conglutinans v. citrinum Wr.

Dolichos biflorus Linn.

* Fusarium solani (Mart.) App. et Wr. v. minus Wr.

Gossypium arboreum Linn.

Fusarium vasinfectum Atk.

Lycopersicon esculentum Mill.

Fusarium semitectum Berk. & Rav.
F. equiseti (Corda) Sacc. v. bullatum (Sherb.) Wr.
F. scirpi Lamb. et Fautr.
* F. solani (Mart.) App. et Wr. v. minus Wr.
* F. solani (Mart.) App. et Wr. v. striatum (Sherb.) Wr.

Musa sapientum Linn.

Fusarium semitectum Berk. & Rav.

Oryza sativa Linn.

* Fusarium scirpi Lamb. et Fautr.
* F. scirpi Lamb. et Fautr. v. longipes (Wr. et Rg.) Wr.
F. culmorum (W. G. Sm.) Sacc.

Phaseolus radiatus Linn.

* Fusarium solani (Mart.) App. et Wr. v. minus Wr.

Solanum melongena Linn.

* Fusarium equiseti (Corda) Sacc. v. bullatum (Sherb) Wr.
* F. oxysporum Schlecht.
* F. coeruleum (Lib.) Sacc.
* F. solani (Mart.) App. et Wr. v. martii (App. et Wr.) Wr.
* F. solani (Mart.) App. et Wr..v. minus Wr.
* F. solani (Mart.) App. et Wr. v. striatum (Sherb.) Wr.

Asterisks indicate fungi for which the hosts mentioned are new. *Fusarium equiseti.* v. *bullatum, F. scirpi* v. *longipes* and *F. conglutinans* v. *citrinum* are new records for India.

INTRODUCTION

The present paper is a systematic account of Fusaria isolated from diseased crop plants in the course of a study of South Indian Fusaria taken up a few years ago. Many of the isolates included in this investigation were mentioned in an earliler paper (Subramanian, 1951) wherein the question of "wild type" in the genus was discussed. The isolates were then referred to the various sections according to the classification of Wollenweber & Reinking (1935). Subsequent work has resulted in determining the specific identity of the majority of these and other isolates. In the following account the classification of Wollenweber & Reinking (1935) is followed.

METHODS

The method of isolation of Fusaria was as follows: bits of infected material were surface sterilized in 1/1000 acqueous mercuric chloride for 40-50 seconds and washed thoroughly in several, changes of sterilised water and then plated out on acidified potato

dextrose agar in Petri dishes. After preliminary transfer of the fungus to agar slants in test tubes, single spore cultures were obtained in each case and maintained on potato dextrose agar.

The isolates were studied immediately after isolation since the majority of them were in a state of "hochkultur" (see Subramanian, 1951) soon after isolation when grown on potato dextrose or oatmeal agar. Replicate cultures were used in every case.

FUSARIA ISOLATED FROM CROP PLANTS

The species are listed under the sections in which they have been placed by Wollenweber & Reinking (1935). Measurements of conidia and chlamydospores are given in microns.

SECTION SPOROTRICHIELLA

Microconidia 0-1-septate, spherical-ovoid, lemon-, pear-shaped, or fusiform or elliptical. In the species *F. chlamydosporum* and *F. poae* macroconidia are few and are scattered in the aerial mycelium; in *F. sporotrichioides* and *F. tricinctum* they are usually abundant and are produced in sporodochia and pionnotes. Macroconidia resemble those of the section *Roseum*. Unlike section *Roseum*, however, chlamydospores are produced in abundance. Colour of stroma carmine to purple red or ochre yellow.

Fusarium chlamydosporum Wr. et Rg.

Wollenweber & Reinking, Phytopathology, 15: 156. 1925.—Reinking & Wollenweber, 1927, Philipp. J. Sci., 32: 115, ic; Wollenweber, 1931, Z. Parasitenk., 3: 475; Wollenweber & Reinking, 1935, Die Fusarien, p. 47, ic.; Die Verbreitung der Fusarien in der Natur, p. 19.; Doidge, E.M., 1938, Bothalia, 3: 346, i.c.; Wollenweber, 1943, Zbl. Bakt., Abt. II, 106: 107, 128.; Subramanian, C. V., 1952, Proc. Nat. Inst. Sci. India, 18: 561, ic.

Wollenweber, Fus. del. 883.

Microconidia oval or pyriform, mostly non-septate, rarely 1-septate. Macroconidia rare, when present scattered, falcate, 1-3-septate; sporodochia none; mycelium floccose; growth on substratum plectenchymatous, of various colours, rose to carmine, sulphuric yellow to dark brown; chlamydospores produced prolifically, globose or pyriform, terminal or intercalary, occurring singly, in pairs, mostly in chains and clusters, 8-16 in diameter. The abundance of large chlamydospores is a characteristic of the species.

Isolated from damped-off seedlings of *Coriandrum sativum* Linn. (Umbelliferae) grown in Udamalpet black cotton soil in pots, University Botany Laboratory, Madras. Not so far reported on this host.

On potato dextrose agar: growth fluffy and cottony, with the mycelium white or coloured with various shades of pink and cream to yellow. Sporodochia and pionnotes none.

Measurements of Conidia

0-septate	7·7 × 3 mostly 4-9 × 2·5 (4-13 × 1-4)
1-septate	13 × 3·3
3-septate	26 × 3·3

SECTION ROSEUM

Macroconidia subulate, thin-walled, slender, falcate to almost straight, cylindrical and of even diameter for a considerable part of their length, tapering gradually to both ends, apical cell long, sometimes narrow filiform, base more or less pedicellate; orange coloured or lighter in mass, brick-red or reddish brown when dry; macroconidia borne on the stroma, or in pionnotes and sporodochia, or else scattered in the aerial mycelium or in false heads. Chlamydospores none; blue sclerotia may or may not be present. Mycelial and stromatic colours developed are: pale white, rose, purple, carmine and yellow.

F. avenaceum (Fr.) Sacc.

Saccardo, 1886, Syll. Fung. 4: 713; Lindau, 1909, in Rabh. Kryptogamenflora, I, 9: 540; Wollenweber, 1917, Ann. mycol., 15: 15; Bennett, F. T., 1928, Ann. appl. Biol., 15: 229, ic.; Wollenweber, 1931, Z. Parasitenk., 3: 460, 476.; Wollenweber and Reinking, 1935, Die Fusarien, p. 53, ic.; Die Verbreitung der Fusarien in der Natur, p. 16-18, ic.; Doidge, E. M., 1938, Bothalia, 348, ic.; Wollenweber, 1943, Zbl. Bakt., Abt. II, 106: 107, 132, ic.; Gordon, W. L., 1952, Canad. J. Bot., 30: 221, ic.; Subramanian, C. V., 1952, Proc. Nat. Inst. Sci. India, 18: 562, ic.

Wollenweber, Fus. del. 127, 128, 130-136, 139-161, 163, 164, 178-184, 186-194, 560-568, 572-574, 892, 894-899, 1132, 1133.

Conidia usually in false heads, in sporodochia or pionnotes; in mass orange, becoming darker if drying in a resinous mass, or becoming pink or rose or carmine in a powdery condition; yellow, ochre, and carmine to red brown are the usual stromatic colours;

conidia subulate or filiform, long, sometimes more curved near the apex than in the middle, with pedicellate base, mostly 3-5, rarely 0-2,- 6-7-septate.

Although chlamydospores are stated to be absent in the species (Wollenweber, *Zbl. Bakt.*, Abt. II, 106: 135. 1943), these have been observed by Bennett (*Ann. appl. Biol.*, 15: 230. 1928) and also by Subramanian (1952) in isolates of *Fusarium* agreeing with *F. avenaceum* in all other characters.

Isolated from damped-off seedlings of *Coriandrum sativum* Linn. (Umbelliferae), grown in Udamalpet black cotton soil in pots, University Botany Laboratory, Madras. Not so far reported on this host.

On potato dextrose agar: growth adpressed with little aerial mycelium, slimy in appearance due to production of conidia in a pionnotes. Spore masses cream to salmon-coloured.

Measurements of Conidia

0-septate 11 × 2·7 mostly 8-15 × 2·5 (6-19 × 1-4)
1-septate 20 × 2·7 mostly 16-25 × 2·4-3·4 (11-25 × 2-4)
3-septate 46 × 2·7 mostly 34-54 × 2·5 (29-69 × 2-4)
4-septate 57 × 2·7 mostly 49-59 × 2·5 (39-77 × 2-4)
5-septate 66 × 2·8 mostly 56-70 × 2·5 (49-80 × 2-4)

SECTION ARTHROSPORIELLA

Aerial mycelium profuse, white to pinkish. Conidia produced on branched conidiophores arising from the vegetative hyphae, sometimes grouped in sporodochia or pionnotes. Microconidia apedicellate, fusiform to lanceolate, 0-3-septate. Macroconidia with well-marked foot, falcate, attenuate, 3-many-septate, in mass somewhat ochraceous. Chlamydospores present, intercalary or terminal.

F. semitectum Berk. et Rav.

Berkeley, J. M., 1875, Grevillea, 3: 98.; Saccardo, 1886, Syll. Fung., 4: 718.; Wollenweber, 1917, Ann. mycol., 15: 11.; 1918, Ber. dtsch. bot. Ges., 35: 733.; Wollenweber and Reinking, 1925, Phytopathology, 15: 157.; Reinking and Wollenweber, 1927, Philipp. J. Sci., 32: 118, ic.; Wollenweber, 1931, Z. Parasitenk., 3: 324, ic.; Wollenweber and Reinking, 1935, Die Fusarien, p. 58, ic.; Die Verbreitung der Fusarien in der Natur, p. 36, ic.; Gordon, W. L. 1952, Canad. J. Bot., 30: 222, ic.

Wollenweber, Fus. del. 112, 906, 1135.

Aerial mycelium floccose, white to ochraceous or pale rose in colour. Stroma plectenchymatic. Sporodochia absent. Conidia scattered in the aerial mycelium, spindle-shaped to falcate, with somewhat gradually tapering but bluntly rounded apex, with indistinct foot cell, but often with a sub-papillate base. Conidia mostly 3-septate, smaller conidia (0-1-septate) few. Chlamydospores present, 6-11 in diameter.

Isolated from roots of diseased plants of *Musa sapientum* Linn. (Musaceae) collected from Ernakulam (Travancore-Cochin State); from roots of wilted plants of *Lycopersicon esculentum* Mill. (Solanaceae), collected from the Agricultural Research Institute, Coimbatore (Madras State); from wilted plants of *Amaranthus* sp. (Amaranthaceae), collected from Ernakulam.

Amaranthus is a new host for this species. It is noteworthy that the type host for this species is *Musa sapientum.*

The isolate from Musa sapientum:

On potato dextrose agar: mycelium white to pale pinkish in colour and tufted, with no development of sporodochia or pionnotes, but presenting a powdery appearance.

Measurements of Conidia

0-septate 8·3 × 2·5 (5-12 × 2-4)
1-septate 13 × 3 (10-17 × 2-4)
3-septate 31 × 4·1 (18-33 × 3-5)

The isolate from Lycopersicon esculentum:

On potato dextrose agar: growth similar to the isolate from *Musa sapientum.*

Measurements of Conidia

0-septate 9 × 2·7 (5-14 × 2-4)
1-septate 15 × 3·1 (10-20 × 2-4)
3-septate 33 × 4 (21-37 × 3-5)

The isolate from Amaranthus sp.:

On potato dextrose agar: growth fluffy with development of a pale pink colour. Conidia formed in tufts visible under a lens. Sporodochia none.

Measurements of Conidia

0-septate 8·7 × 3 (5-13 × 2-4)
1-septate 13 × 3·3 (9-18 × 2-4)
3-septate 27 × 4 (20-33 × 3-5)
5-septate 35 × 4·3 mostly 30-39 × 3·3-4·9 (26-44 × 3-5).

F. semitectum Berk. et Rav. v. **majus** Wr.

Wollenweber, 1931, Z. Parasitenk., 3: 325, ic.; Wollenweber and Reinking, 1935, Die Fusarien, p. 59, ic.; Die Verbreitung der Fusarien in der Natur, p. 36, ic.; Doidge, E.M., 1938, Bothalia, 3: 353, ic.; Bugnicourt, F., 1939, Encyclopedie mycol., 11: 48, ic.

Wollenweber, Fus. del. 907-910.

Non-septate conidia few or none, but small 1-3-septate conidia present, mostly spindle-shaped, often exhibiting dorsiventrality having a convex curvature on the dorsal side, falcate or anguiform with a conical rounded apex and a papillate or sub-papillate base. Macroconidia present, longer than the microconidia, dorsiventral and falcate with a papillate or sometimes sub-pedicellate base, with more or less curvature in the middle; apical cell conical and sometimes curved with usually a rounded tip; thin-walled, with rather delicate septa, up to 5-septate. Sporodochia or pionnotes none, macro conidia borne on branched conidiophores. Chlamydospores present, terminal, rarely intercalary, large with usually smooth walls, 1-2-celled or in chains; 1-celled, 9 × 9 (8-10 × 8-10); 2-celled, 15· 8 × 9·8 (13-20 × 8-12).

Isolated from wilted plants of *Cyamopsis tetragonoloba* Taub. (Leguminosae), collected at the Agricultural Research Institute, Coimbatore (Madras State). Not so far reported on this host.

On potato dextrose agar: growth slightly fluffy with orange red tinge at bottom of slant; elsewhere appearance powdery and white, the former due to profuse sporulation; macroconidia borne on highly branched conidiophores.

Measurements of Conidia

0-septate 7 × 2·7 (4-10 × 1-5)
1-septate 13 × 3·1 (9-17 × 2-4)
3-septate 23 × 3·2 mostly 18-25 × 2·5-3·3 (14-32 × 2-6)
4-septate 26 × 3·4 mostly 23-29 × 3·3 (21-32 × 2-5)
5-septate 28 × 3·5 mostly 24-30 × 3·3-4·2 (23-34 × 3-5)

This isolate comes nearest to *F. semitectum* v. *majus,* although the 5-septate conidia are smaller than those described for this variety. The occurrence of terminal rather than intercalary chlamydospores, however, is a point against inclusion of this isolate in section *Arthrosporiella* as conceived by Wollenweber and Reinking (1935, p. 57). Nevertheless, in all other features the isolate so strikingly resembles *F. semitectum* v. *majus* that I have no hesitation in designating the isolate as this species.

SECTION GIBBOSUM

Aerial mycelium white or brownish, less frequently yellow, rose to carmine. Stroma ochre-brown to black-brown, sometimes golden yellow to carmine-red. Microconidia more or less scattered freely in the mycelium, disappearing later. Macroconidia in sporodochia and pionnotes, pale ochraceous to orange or orange red; sometimes macroconidia are also found in false heads in the mycelium. Conidia dorsiventral, sickle-shaped, with parabolic or hyperbolic curvature, sometimes with acutely arched dorsal line and somewhat less curved ventral line, attenuate at both ends, with filiform or flagella-like apical cell, and very definitely pedicellate base, thin-walled, 3-5-7- or more-septate. Chlamydospores intercalary, seldom terminal, in conidia and in mycelium, globose, single or in chains or clusters, brown in mass. Spherical, brown or dark blue sclerotia may or may not be present.

F. equiseti (Corda) Sacc.

Saccardo, 1886, Syll. Fung., 4: 707; Lindau, 1909, in Rabh. Kryptogamenflora, I, 9: 537.; Wollenweber, 1917, Ann. mycol., 15: 15-16.; 1918, Ber dtsch. bot. Ges., 35: 734.: 1931, Z. Parasitenk., 3: 330, ic.; Wollenweber and Reinking, 1935, Die Fusarien, p. 63, ic.; Die Verbreitung der Fusarien in der Natur, p. 22-23.; Bennett, F. T., 1935, Ann. appl. Biol., 22: 487, ic.; Doidge, E. M., 1938, Bothalia, 356, ic.; Bugnicourt, F., 1939, Encyclopedie mycol., 11: 60, ic.; Wollenweber, 1943, Zbl. Bakt., Abt. II, 106: 108, ic.; Gordon, W. L., 1952, Canad. J. Bot., 30: 225, ic.; Subramanian, C. V., 1952, Proc. Nat. Inst. Sci. India, 18: 564, ic.

Wollenweber, Fus. del. 202-208, 210, 211, 596, 597, 919, 920.

Conidia few at first, scattered in the white to yellowish, or pink mycelium, 1-2-celled, oval or oblong to fusiform-falcate, disappearing when the typical macroconidia begin to develop. Stroma pale or brown. Macroconidia produced in sporodochia or pionnotes, less frequently scattered in the aerial mycelium, in mass at

first pale, then ochre to salmon pink; fusiform-falcate, thick in the middle and gradually tapering at either end, with parabolic curvature, straight or bent at the apex, tapering to a fine point, base pedicellate; dorsal side usually more markedly curved than the ventral; septa more or less equidistant, seldom more closely crowded in the middle than at the ends; mostly 5-septate, seldom 3-4-, exceptionally up to 7-septate. Chlamydospores present, globose, smooth or rough, intercalary, seldom terminal, 1-celled, in chains or clusters, brown in mass, 8-14 in diameter.

Isolated from damped-off seedlings of *Coriandrum sativum* Linn. (Umbelliferae), grown in Udamalpet black cotton soil in pots, University Botany Laboratory, Madras. Not so far reported on this host.

On potato dextrose agar: growth fluffy with white aerial mycelium; sporodochia salmon coloured.

Measurements of Conidia

0-septate 9 × 2·7 (5-20 × 2-4)
1-septate 13 × 3 (9-20 × 2-4)
3-septate 32 × 3·8 (18-43 × 2-5)
5-septate 42 × 4·7 mostly 34-47 × 3·3-5·8 (31-51 ×3-7)
7-septate 47 × 4·8

F. equiseti (Corda) Sacc. v. **bullatum** (Sherb.) Wr.

Wollenweber, 1931, Z. Parasitenk., 3: 331, ic.; Wollenweber and Reinking, 1935, Die Fusarien, p. 64, ic.; Die Verbreitung der Fusarien in der Natur, p. 23; Doidge, E. M., 1938, Bothalia, 3: 359, ic.; Bugnicourt, F., 1939, Encyclopedie mycol., 11: 64, ic.; Wollenweber, 1943, Zbl. Bakt., Abt. II, 106: 108, ic.

Wollenweber, Fus. del. 117, 209, 913-918.

Microconidia none. Macroconidia present, abundant, often in pionnotes, up to 5-septate, typically thin-walled, dorsiventral, more or less falcate, with parabolic (sometimes hyperbolic) curvature, tapering at both ends and broader at the middle, base markedly pedicellate with well-defined foot, apex smoothly bent or at an angle, septa thin and usually equidistant, the basal and the apical cells longer and narrower than the middle ones; apical cell also longer than the basal one. Conidia produced in light ochre-coloured sporodochia or pionnotes. Chlamydospores present, not abundant, intercalary or terminal, 1-2-celled, sometimes in chains and knots, round, oval or pear-shaped; 1-celled 8·9 × 7·5 (6-12 × 6-9); 2-celled 14 × 8 (11-17 × 6-9).

Isolated from roots of wilted plants of *Solanum melongena* Linn. (Solanaceae) and from wilted plants of *Lycopersicon esculentum* Mill. (Solanaceae), collected at the Agricultural Research Institute, Coimbatore (Madras State). *Solanum melongena* is a new host for the fungus.

The isolate from Solanum melongena:

On potato dextrose agar: aerial mycelium profuse, mostly white in colour; stroma pale to brown, the substratum often tinged with the colour of the stroma.

Measurements of Conidia

2-septate	32 × 4·2		
3-septate	34 × 3·7	mostly 31-37 × 3·3-4·2	(26-42 × 3-5)
4-septate	36 × 3·9	mostly 33-38 × 3·3-4·2	(33-45 × 3-5)
5-septate	42 × 3·9	mostly 38-45 × 3·3-4·2	(34-54 × 3-5)

The isolate from Lycopersicon esculentum:

On potato dextrose agar: growth similar to that of the isolate from *Solanum melongena.*

Measurements of Conidia

2-septate	30 × 4·1		
3-septate	35 × 3·9	mostly 31-38 × 3·3-4·2	(29-43 × 3-5)
4-septate	36 × 3·9	mostly 31-39 × 3·3-4·2	(32-46 × 3-5)
5-septate	41 × 3·9	mostly 37-43 × 3·3-4·2	(33-51 × 3-5)

F. scirpi Lamb. et Fautr.

Saccardo, 1895, Syll. Fung., 11: 651.; Wollenweber, 1917, Ann. mycol., 15: 16.; 1931, Z. Parasitenk., 3: 334, i.c.; Wollenweber & Reinking, 1935, Die Fusarien, p.66, i.c.; Die Verbreitung der Fusarien in der Natur, p. 34-35, i.c.; Diodge, E.M., 1938, Bothalia, 3: 360, i.c.; Wollenweber, 1943, Zbl. Bakt., Abt. II, 106: 109, i.c.; Subramanian, C.V., 1952, Proc. Nat. Inst. Sci. India, 18: 566, i.c.

Wollenweber, Fus. del. 198-201, 212-218, 595, 598, 922, 926-929, 1137.

Typical non-septate microconidia few, when present oval in shape. Macroconidia in sporodochia; dorsiventral and falcate, typically thin-walled with delicate septa, having a parabolic curvature, base markedly pedicellate, curved or bent at an angle at the apex

forming a rather long apical cell which tapers to a rounded point; conidium broader nearer the apex and narrowing down below to a foot-cell; up to 7-, but commonly 5- or 3-5-septate. Chlamydospores present, smooth-walled, intercalary, 1-2-celled, also in chains; 1-celled 13 × 13; 2-celled 16·8 × 9·5 (13-22 × 7-12).

Isolated from roots of wilted plants of *Cyamopsis tetragonoloba* Taub. (Leguminosae), from wilted plants of *Lycopersicon esculentum Mill.* (Solanaceae), and from diseased plants of *Oryza sativa* Linn. (Gramineae), collected from the Agricultural Research Institute, Coimbatore (Madras State). *Cyamopsis tetragonoloba* and *Oryza sativa* are two new hosts for this species.

The isolate from Cyamopsis tetragonoloba:

On potato dextrose agar: growth white consisting of a compact layer, with some aerial mycelium on top of slant. Sporodochial and pionnotal development present, but not abundant.

Measurements of Conidia

0-septate 7 × 2·9
3-septate 34 × 3 (18-45 × 2-4)
4-septate 37 × 3·1 (24-49 × 2-4)
5-septate 47 × 3·4 mostly 33-59 × 3·3 (28-67 × 2-5)
6-septate 54 × 3·6 mostly 53-62 × 3·3-4·2 (44-69 × 3-5)

The isolate from Lycopersicon esculentum:

On potato dextrose agar: growth adpressed with no aerial mycelium: profuse sporulation in sporodochia and pionnotes of a buff colour.

Measurements of Conidia

0-septate 6 × 2·9 mostly 5-8 × 2·5-3·3 (4-9 × 2-4)
3-septate 42 × 3·3 (38-45 × 3-4)
4-septate 44 × 3·3 (39-49 × 3-5)
5-septate 54 × 3·6 mostly 49-59 × 3·3-4·2 (36-67 × 2-5)
6-septate 57 × 3·5 mostly 53-62 × 3·3-4·2 (48-69 × 3-5)

The isolate from Oryza sativa

On potato dextrose agar: growth slightly fluffy with white aerial mycelium; sporodochia of a salmon colour developed.

Measurements of Conidia

0-septate 8 × 2·6 (4-11 × 2-4)
3-septate 39 × 3·7 (35-43 × 3-5)

4-septate 41 × 3·7 (35-49 × 3-5)
5-septate 47 × 3·6 mostly 43-49 × 3·3-4·2 (39-54 × 3-5)
6-septate 52 × 3·6 mostly 47-58 × 3·3-4·2 (43-69 × 3-5)

F. scirpi Lamb. et Fautr. v. **longipes** (Wr. et Rg.) Wr.

Wollenweber, 1931, Z. Parasitenk., 3: 337.; Wollenweber & Reinking, 1935, Die Fusarien, p. 68.; Die Verbreitung der Fusarien in der Natur, p. 36.; Bugnicourt, F., 1939, Encyclopedie mycol., 11: 73, ic.

Wollenweber, Fus. del. 937.

Conidia produced in sporodochia and pionnotes, ochraceous to orange coloured in mass, markedly elongate and falcate, parabolically or hyperbolically curved, attenuate with whip-like apical portion which may be very much curved or twisted frequently, with long, pedicellate basal cell, mostly 5- (4-6-) septate. Chlamydospores present, mostly intercalary, 6-10 in diameter.

Isolated from diseased plants of *Oryza sativa* Linn. (Gramineae), collected at the Agricultural Research Institute, Coimbatore. Not so far reported on this host.

On potato dextrose agar: mycelium somewhat purple coloured, compact and velutinous, with formation of pionnotal and sporodochial masses in patches.

Measurements of Conidia

4-septate 57 × 2·9
5-septate 69 × 3 (53-95 × 2-5)
6-septate 97 × 3·2 (85-110 × 3-5)

SECTION DISCOLOR

Macroconidia comparatively thick-walled, fusiform to sickle-shaped, tapering at both ends, curved (dorsal side convex, ventral side less curved, usually concave but sometimes somewhat convex); apex constricted like the neck of a bottle, curved and rostrate, or conical to truncate or rounded; base pedicellate when fully developed and mature. Sporodochia and pionnotes ochre, salmon pink or orange. Some species have small or medium-sized conidia, which are pedicellate, 0-3- or more-septate, oval, fusiform to cylindrical, straight or curved; these may predominate or may disappear when sporodochia are formed. Other species have some comparatively slender conidia. The stroma is flat, effuse, plectenchymatous, scle-

rotially erumpent in places, and coloured variously: pale, carmine to purple, red, yellow, brown or rarely blue; in a few it is pale and homogeneous. Spherical sclerotia may or may not be present; when present, they are blue, brown or colourless. Aerial mycelium well-developed, white, pink, or tinged with the colour of the stroma. Chlamydospores few, terminal or intercalary, single, in chains or clusters, brown in mass.

F. culmorum (W. G. Sm.) Sacc.

Saccardo, 1895, Syll. Fung., 11: 651.; Wollenweber, 1914, J. agric. Res., 2: 260, i.c.; 1917, Ann. mycol., 15: 21.; Sherbakoff, 1915, Cornell Univ. agric. Exp. Sta. Mem., 6: 240.; Bennett, F.T., 1928, Ann. appl. Biol., 15: 225, i.c.; Wollenweber, 1931, Z. Parasitenk., 3: 360, i.c.; Wollenweber & Reinking, 1935, Die Fusarien, p. 79, i.c.; Die Verbreitung der Fusarien in der Natur, p. 21; Doidge, E.M., 1938, Bothalia, 3: 380, i.c.; Wollenweber, 1943, Zbl. Bakt., Abt. II, 106: 108, i.c.; Gordon, W.L., 1952, Canad. J. Bot., 30: 227, i.c.; Subramanian, C.V., 1952, Proc. Nat. Inst. Sci. India, 18: 570, ic.

Wollenweber, Fus. del. 330-337, 613, 943-945, 1147-1149.

Conidia at first scattered in the aerial mycelium, or in false heads, sometimes forming a pionnotal layer, or produced in sporodochia; coloured variously in mass, yellow, pink, then ochre to coffee brown, often becoming more or less tinged with the purple red or golden yellow to ochre brown colour of the stroma. Conidia spindle to sickle-shaped, gradually or abruptly attenuate at both ends; apical cell sometimes rostrate, constricted like the neck of a bottle, base pedicellate, wall thick, and with distinct septa; 5-septate, less frequently 3-4- or 6-septate. Chlamydospores mostly intercalary, globose or oval, in conidia and in mycelium, single, 2-celled, or in chains and clusters, brown in mass, 1-celled 9-14, 2-celled 16-22 × 8-17.

Isolated from roots of diseased plants of *Oryza sativa* Linn. (Gramineae), collected at the Agricultural Research Institute, Coimbatore (Madras State).

On potato dextrose agar: growth white and fluffy, with formation of cream or salmon coloured sporodochia; substratum coloured rose to pinkish.

Measurements of Conidia

3-septate	33 × 5·5	mostly 27-42 × 4·9-6·6	(22-45 × 4-7)
4-septate	35 × 5·7	mostly 26-47 × 4·9-6·6	(25-50 × 4-7)
5-septate	37 × 6·0	mostly 30-43 × 4·9-6·6	(29-55 × 4-7)

SECTION ELEGANS

Micro- and macroconidia present. Microconidia oval, ellipsoidal, kidney-shaped or straight, 5-12 × 2·2-3·5, single on free conidiophores, or in false heads, produced in abundance. Macroconidia in sporodochia or pionnotes, but sometimes produced scattered in the aerial mycelium. Conidial masses usually formed on an erumpent or flat, plectenchymatous or sclerotial stroma. In some species the macroconidia are elongated, fusiform to subulate, tapering at both ends or slightly constricted; in others they are fusiform-falcate, usually constricted and abruptly curved at the apex, and pedicellate or papillate at the base. Macroconidia dorsiventral to almost cylindrical, thin-walled, usually with 3, sometimes up to 5, delicate septa, 3-septate 27-46 × 3-5, 5-septate 50-60 × 3-5; in mass pale, isabellinous, brownish white, flesh colour to salmon orange. Mycelium white or tinged with the colour of the stroma. Stroma pale or pink, orange or purple red, plectenchymatous, effused or raised, more or less erumpent or sclerotial. Chlamydospores abundant, terminal and intercalary, in mycelium and conidia. Sclerotia sometimes present, rough, brown, blue, pale.

F. oxysporum Schlecht.

Saccardo, 1886, Syll. Fung., 4:705.; Lindau, 1909, in Rabh. Kryptogamenflora, I, 9: 525; Wollenweber, 1913, Phytopathology, 3:28, ic.; 1914, J. agric. Res., 2:268; Sherbakoff, 1915, Cornell Univ. agric. Exp. Sta. Mem., 6:220, ic.; Wollenweber, 1917, Ann. mycol., 15:24; Reinking & Wollenweber, 1927, Philipp. J. Sci., 32:187, ic.; Wollenweber, 1931, Z. Parasitenk., 3:416, ic; Wollenweber & Reinking, 1935, Die Fusarien, p. 117, ic.,; Die Verbreitung der Fusarien in der Natur, p. 31, ic., Doidge, E. M., 1938, Bothalia, 3:421, ic.; Wollenweber, 1943, Zbl. Bakt., Abt. II, 106:109, ic.; Gordon, W. L., 1952, Canad. J. Bot., 30:236, ic.; Subramanian, C. V., 1952, Proc. Nat. Inst. Sci. India, 18: 576, ic.

Wollenweber, Fus. del. 378, 1005-1007, 1170-1174.

Stroma brownish white to violet, plectenchymatous, smooth, effuse. Under humid conditions aerial mycelium may be present over the stroma, sporodochia or pionnotes being formed later. Microconidia 1-2-celled, oval to kidney-shaped, abundant, scattered in the aerial mycelium or in false heads. Macroconidia 3- (4-5)-septate, spindle- to sickle-shaped, curved or almost straight, definitely or weakly pedicellate. Chlamydospores terminal and intercalary, globose, smooth rugulose, 1-celled 5-10 in diameter, 2-celled 8-14 × 5-9.

Isolated from roots of wilted plants of *Solanum melongena* Linn. (Solanceae), and from roots of wilted plants of *Cyamopsis tetragonoloba* Taub. (Leguminosae), collected from the Agricultural Research Institute, Coimbatore (Madras State). Not so far reported on these two hosts.

The isolate from Solanum melongena:

On potato dextrose agar: growth consisting of brilliant white, fluffy, compact mycelium; stroma pale white.

Measurements of Conidia

0-septate 10 × 3·1 mostly 8-12 × 2·5-3·3 (6-14 × 2-5)
1-septate 16 × 3·8 mostly 13-19 × 3·3-4·2 (11-22 × 3-5)
2-septate 24 × 4·1 mostly 21-25 × 4·2 (19-27 × 3-5)
3-septate 30 × 4·4 mostly 26-34 × 4·2-4·9 (23-37 × 4-5)
4-septate 38 × 4·8 (34-42 × 4-5)

The isolate from Cyamopsis tetragonoloba:

On potato dextrose agar: mycelial growth loosely fluffy, with slight pinkish tinge in the mycelium; stromatic colour pink.

Measurements of Conidia

0-septate 8 × 3·1 mostly 7-9 × 2·5-3·3 (6-11 × 2-4)
1-septate 10 × 2·5
3-septate 29 × 3·6 mostly 23-34 × 3·3-4·2 (19-30 × 2-5)
4-septate 34 × 3·7

F. conglutinans v. citrinum Wr.

Wollenweber, 1931, Z. Parasitenk., 3: 407.; Wollenweber and Reinking, 1935, Die Fusarien, p. 111.; Die Verbreitung der Fusarien in der Natur, p. 21.

Wollenweber, Fus. del. 358.

Microconidia present, one-celled, oval to ellipsoid, often slightly curved, produced in false heads. Macroconidia dorsiventral with convex curvature on the dorsal side, with pedicellate base, the apical cell curved and narrowed into a conical rounded tip; up to 3-septate, thin-walled and with delicate septa. Chlamydospores present, abundant, terminal or intercalary, 1-2-celled, when 1-celled mostly oval or pear-shaped, with smooth walls: 1-celled 7·7 × 6·4 (5-10 × 5-8); 2-celled 11 × 7 (9-14 × 4-9).

Isolated from roots of wilted plants of *Cyamopsis tetragonoloba* Taub. (Leguminosae), collected at the Agricultural Research Institute, Coimbatore (Madras State). Not reported on this host before.

On potato dextrose agar: growth consisting of scanty aerial mycelium; stroma of a pale dull colour; sporodochia and pionnotes none.

Measurements of Conidia

0-septate 9 × 2·7 mostly 8-12 × 2·4-3·3 (4-14 × 2-4)
1-septate 18 × 3·3
3-septate 26 × 3·5 mostly 24-27 ×3·3-4·2 (19-29 × 3-5)

F. orthoceras App. et Wr.

Appel and Wollenweber, 1910, Arb. biol. Reichsanst Land. u. Forstw., 8: 141-56, ic.; Saccardo, 1913, Syll. Fung., 22: 1477.; Wollenweber, 1913, Phytopathology, 3: 30; 1914, J. agric. Res., 2: 263-64.; Lewis, 1913, Maine agric. Exp. Sta. Bull., 219: 256.; Sherbakoff, 1915, Cornell Univ. agric. Exp. Sta. Mem., 6: 202-203, ic.; Wollenweber, 1917, Ann. mycol., 15: 23.; Reinking and Wollenweber 1927, Philipp. J. Sci., 32: 179, ic.; Wollenweber, 1931, Z. Parasitenk., 3: 408, ic.; Wollenweber, and Reinking, 1935, Die Fusarien, p. 111, ic.; Die Verbreitung der Fusarien in der Natur, p. 30, ic.; Doidge, E.M.; 1938, Bothalia, 3: 405, ic.

Wollenweber, Fus. del 360-362, 620, 621, 985-989.

Microconidia present, small, mostly non-septate, oval to ellipsoid or sometimes curved and kidney-shaped, scattered in the aerial mycelium or borne in false heads. Macroconidia dorsiventral and falcate, typically thin-walled and with delicate septa, up to 5-septate, but commonly 3-septate, slightly curved or almost cylindrical in the middle, but curved at one end into an apical cell with a narrowly and smoothly rounded tip; basal cell pedicellate. Chlamydospores present, abundant, 1-2-celled, mostly terminal; when 1-celled mostly globose but sometimes oval or pear-shaped; 1-celled 7·9 × 7·9 (6-10 × 6-10), 2-celled 12 × 8 (9-15 × 7-9).

Isolated from roots of wilted plants of *Cicer arietinum* Linn. (Leguminosae) grown in Udamalpet black cotton soil in pots, University Botany Laboratory, Madras.

On potato dextrose agar: growth mat-like; mycelium of a pale dull colour; stromatic colour pale dull to cream; sporodochia and pionnotes absent.

Measurements of Conidia

0-septate 8 × 2·9 mostly 6-10 × 2-4-3·3 (4-12 × 2-4)
1-septate 15 × 3·7 (11-17 × 2-4)
3-septate 30 × 3·7 mostly 26-35 × 3·3-4·2 (21-39 × 3-5)
4-septate 33 × 3·6
5-septate 37 × 4·2

F. vasinfectum Atk.

Atkinson, G. F., 1892, Alabama agric. Exp. Sta. Bull., 41: 19, ic.; Lindau, 1909, in Rabh. Kryptogamenflora, I, 9: 563.; Saccardo, 1913, Syll. Fung., 22: 1481.; Wollenweber, 1913, Phytopathology, 3: 29.; 1917, Ann. mycol., 15: 24; 1931, Z. Parasitenk., 3: 423-25, ic.; Wollenweber and Reinking, 1935, Die Fusarien, p. 124-26, ic.; Die Verbreitung der Fusarien in der Natur, p. 39-40.; Doidge, E.M., 1938, Bothalia, 3: 432, ic.; Bugnicourt, F., 1939, Encyclopedie mycol., 11: 114, ic.; Wollenweber, 1943, Zbl. Bakt., Abt. II, 106: 110, ic.; Subramanian, C. V., 1952, Proc. Nat. Inst. Sci. India, 18: 273-85, ic., 573.

Wollenweber, Fus. del. 376.

Isolated from wilted plants of *Gossypium arboreum* Linn. (Malvaceae), collected from Udamalpet, Coimbatore District (Madras State).

Details of the isolates are given elsewhere (Subramanian, 1952a, 1952b).

F. udum Butler

Butler, E. J., 1910, Mem. Dept. Agric. India, Bot. Ser., II (9): 54, ic.; 1918, Fungi and Disease in Plants, p. 247-49, ic.; Saccardo, 1913, Syll. Fung., 22: 1479.; Wollenweber, 1938, Arb. biol. Reichsanst. Land—u. Forstw., 22: 339-47.; Padwick, G. W., 1941, Indian J. agric. Sci., 11: 672, ic.

Microconidia present, abundant, usually one-celled, small, mostly curved and kidney-shaped, often mamillate at the base. Macroconidia dorsiventral and falcate, with curvature and characteristic shape, long and narrow, typically thin-walled with very delicate septa which are equidistant, up to 5-septate, but more commonly 3-septate, markedly curved at one end into a somewhat hooked apical cell, basal cell pedicellate or sub-pedicellate. True chlamydospores not observed even in old cultures.

Isolated from wilted plants of *Cajanus cajan* (Linn.) Millsp. (Leguminosae), collected at the Agricultural Research Institute, Coimbatore, and from the University Botany Laboratory campus, Madras.

On potato dextrose agar: growth adpressed, with the appearance on the agar surface oily due to profuse development of pionnotal slime; spore masses salmon coloured.

Measurements of Conidia

0-septate 9 × 2·6 mostly 7-10 × 2·5 (5-11 × 2-4).
1-septate 13 × 2·7 mostly 9-15 × 2·5 (9-19 × 2-4)
3-septate 32 × 3 mostly 26-39 × 2·5-3·3 (24-44 × 2-4).

SECTION MARTIELLA

Micro- and macroconidia present. Microconidia mostly 1-celled, small, oval to oblong. Macroconidia dorsiventral, spindle- to sickle-shaped, thick-walled, pluriseptate, septa distinct; curvature more decided near the apex and slight in the central part of the conidium, apex rounded or tapering; base pedicellate or mamillate. The median diameter of the conidia is of diagnostic value in this section. Conidial masses pale, white, yellowish or brownish, or in older cultures darker, honey-coloured to amber, or becoming tinged with the colour of the stroma. Stroma yellow brown to dark blue. Sclerotial bodies, when present, brown, green, violet or blue-black. Chlamydospores abundant, terminal or intercalary, 1-2-celled, in chains or clusters, smooth or rough.

F. coeruleum (Lib.) Sacc.

Saccardo, 1886, Syll. Fung., 4: 705.; Lindau, 1909, in Rabh. Kryptogamenflora, I, 9: 574.; Appel and Wollenweber, 1910, Arb. biol. Anst. f. Land-u. Forstw., 8: 84-91, ic.; Wollenweber, 1913, Phytopathology, 3: 31, 44, 45, ic.; Carpenter, 1915, J. agric. Res., 5: 204, ic.; Sherbakoff, Cornell Univ. agric. Exp. Sta. Mem., 6: 620, ic.; Pethybridge and Lafferty, 1917, Scient. Proc. roy. Dublin Soc., n.s., 21: 193-222, ic.; Wollenweber, 1917, Ann. mycol., 16: 25.; 1931, Z. Parasitenk., 3: 451, ic.; Wollenweber and Reinking, 1935, Die Fusarien, p. 134, ic.; Die Verbreitung der Fusarien in der Natur, p. 20.; Doidge, E. M., 1938, Bothalia, 3: 453, ic.; Jamalainen, E. A., 1943, Über die Fusarien Finnlands II, Valt Maatalousk Julk., 123: 19, ic.; Wollenweber, 1943, Zbl. Bakt., Abt. II, 106: 176, ic.

Wollenweber, Fus. del. 407-410.

Microconidia present, mostly one-celled, oval to oblong, and often slightly curved. Macroconidia dorsiventral, falcate, almost cylindrical in the middle but curved at one end to form a smooth and rounded apex; thick-walled with distinct septa; basal cell mamillate and narrower than the body of the conidium; septa equidistant or not, basal and apical cells invariably shorter than the middle ones. Chlamydospores present, terminal or intercalary, 1-2-celled or in chains, thick-walled, often with corrugations, round or oval in shape; 1-celled 11 × 9 (8-14 × 8-10), 2-celled 13·8 × 9·8 (13-20 × 8-12).

Isolated from roots of wilted plants of *Solanum melongena* Linn. (Solanaceae), collected at the Agricultural Research Institute, Coimbatore; from roots of wilted plants of *Ananas sativus* Schult. (Bromeliaceae), collected at the Agricultural Research Station, Kovilpatti, Tinnevelly District (Madras State). Not so far reported on these two hosts.

The isolate from Solanum melongena:

On potato dextrose agar: growth white, and loosely fluffy in patches. Macroconidia very abundant, produced in large sporodochia of a mm. or less than a mm. in size and of a pale white colour.

Measurements of Conidia

0-septate 11 × 3·9 mostly 9-12 × 3·3-4·2 (7-14 × 3-5)
1-septate 16 × 4 mostly 14-20 × 3·3-4·2 (13-22 × 3-5)
2-septate 27 × 4·2
3-septate 35 × 4·9 mostly 31-39 × 4·9 (28-42 × 4-6)
4-septate 39 × 5·1 mostly 36-42 × 4·9 (31-44 × 4-6)
5-septate 42 × 4·9 mostly 41-44 x 4·9 (39-45 × 4-6).

The isolate from Ananas sativus:

On potato dextrose agar: growth pale white with formation of pale coloured sporodochia.

Measurements of Conidia

0-septate 10 × 3·7 mostly 8-13 × 3·3-4·2 (7-14 × 3-5)
1-septate 13 × 3·8
3-septate 36 × 4·9 mostly 31-40 × 4·9 (27-42 × 4-6)
4-septate 39 × 5·1
5-septate 41 × 4·9 mostly 39-44 × 4·9 (37-46 × 4-6)

F. javanicum Koorders

Koorders, 1907, Verh. Koninkl. Akad. Wetensch. Amsterdam, II, 13: 247, ic.; Saccardo, 1913, Syll. Fung., 22: 1482.; Wollenweber, 1917, Ann. mycol., 15: 26.; Reinking and Wollenweber, 1927, Philipp. J. Sci., 32: 232, ic.; Wollenweber, 1931, Z. Parasitenk., 3: 452, 483.; Wollenweber and Reinking, 1935, Die Fusarien, p. 131, ic.; Die Verbreitung der Fusarien in der Natur, p. 25, ic.; Doidge, E.M., 1938, Bothalia, 3: 443, ic.; Bugnicourt, F., 1939, Encyclopedie mycol., 11: 125, ic.; Wollenweber, 1943, Zbl. Bakt., Abt. II, 106: 108, 178, ic.; Subramanian, C. V., 1952, Proc. Nat. Inst. Sci. India, 18: 574, ic.

Wollenweber, Fus. del. 349, 424, 426-428, 1025-1027.

Microconidia present, usually 1-celled, oval to oblong in shape, small. Macroconidia dorsiventral and falcate, thick-walled with well-defined septa, up to 5-, but more commonly 3-4-septate, septa mostly equidistant, curved at one end and narrowed to form a smoothly rounded apex, apical cell being shorter than other cells; basal cell somewhat triangular and pedicellate, shorter than the intermediate cells, produced mostly in cream-coloured sporodochia. Chlamydospores terminal or intercalary, 1-2-celled, also in chains; 1-celled ones globose or oval or pear-shaped, smooth-walled or verrucose, often borne terminally at the tips of germ tubes of germinated conidia; 1-celled 9 × 9 (8-12 × 8-12), 2-celled 13·8 × 8·7 (11-17 × 8-10).

Isolated from roots of wilted plants of *Ananas sativus* Schult. (Bromeliaceae), collected at the Agricultural Research Station, Kovilpatti, Tinnevelly District (Madras State). Not so far reported on this host.

On potato dextrose agar: growth pale white with some aerial mycelium and good development of sporodochia of a pale dull white colour.

Measurements of Conidia

0-septate 11 × 3·4 mostly 9-14 × 3·3 (6-17 × 2-5)
1-septate 15 × 3·4 mostly 13-17 × 3·3 (9-20 × 2-5)
3-septate 41 × 4·9 mostly 38-45 × 4·9 (33-47 × 4-5)
4-septate 42 × 4·9 mostly 39-45 × 4·9 (38-47 × 4-5)
5-septate 45 × 4·9

F. solani (Mart.) App. et Wr. v. **martii** (App. et Wr.) Wr.

Wollenweber, 1931, Z. Parasitenk., 3: 451, 483.; Wollenweber and Reinking, 1935, Die Fusarien, p. 136, ic.; Die Verbreitung der Fusarien in der Natur, p. 37; Bugnicourt, F., 1939, Encyclopedie mycol., 11: 145, ic.; Wollenweber, 1943, Zbl. Bakt., Abt. II, 106: 110, 182.; Subramanian, C. V., 1952, Proc. Nat. Inst. Sci. India 18: 579, ic.

Wollenweber, Fus. del. 411-414, 1034, 1195, 1196.

Microconidia present, oval to oblong in shape, mostly 1-celled, rarely curved. Macroconidia dorsiventral and falcate, thick-walled and with distinct septa, curvature more evident on the dorsal side; apical cell shorter than the others, somewhat conical with a rounded tip, basal cell pedicellate or sub-pedicellate; septa equidistant or rarely not so; up to 5-, commonly 3-4-septate. Chlamydospores present, abundant, terminal or intercalary, mostly terminal, 1-2-celled, often in short chains or small knots, globose to pear-shaped. Invariably the conidia germinate to give rise to 1-2-celled chlamydospores. Chlamydospores: 1-celled $9{\cdot}2 \times 9{\cdot}2$ (7-11 × 7-11), 2-celled $15 \times 9{\cdot}9$ (13-19 × 8-12).

Isolated from roots of wilted plants of *Solanum melongena* Linn. (Solanaceae), collected at the Agricultural Research Institute, Coimbatore, and from roots of wilted plants of *Cicer arietinum* Linn. (Leguminosae) grown in Udamalpet black cotton soil in pots, University Botany Laboratory, Madras. *Solanum melongena* is a new host for this fungus.

The isolate from Solanum melongena:

On potato dextrose agar: growth adpressed with little aerial mycelium; greenish blue stroma present; sporodochial development profuse.

Measurements of Conidia

0-septate $11 \times 3{\cdot}5$ mostly 8-12 × 3·3-4·2 (8-15 × 2-5)
1-septate $19 \times 4{\cdot}1$ mostly 14-20 × 4·2 (14-24 × 3-5)
2-septate $24 \times 4{\cdot}3$ mostly 23-25 × 4·2 (21-27 × 4-5)
3-septate $36 \times 4{\cdot}9$ mostly 31-44 × 4·9 (24-47 × 4-6)
4-septate $42 \times 5{\cdot}2$ mostly 38-45 × 4·9-5·8 (36-49 × 4-6)
5-septate $50 \times 5{\cdot}8$

The isolate from Cicer arietinum:

On potato dextrose agar: growth similar to that of the isolate from *Solanum melongena*,

Measurements of Conidia

0-septate 13 × 3·4 mostly 11-15 × 3·3 (8-17 × 2-5)
1-septate 21 × 4·4 (16-29 × 3-5)
2-septate 36 × 4·2 mostly 31-39 × 3·3-4·9 (26-42 × 3-5)
3-septate 41 × 4·7 mostly 38-44 × 4·2-4·9 (31-49 × 4-5)
4-septate 46 × 4·6 mostly 43-49 × 4·2-4·9 (41-57 × 4-5)

F. solani (Mart.) App. et Wr. v. **minus** Wr.

Wollenweber, 1917, Ann. mycol., 15: 55.; Saccardo, 1931, Syll. Fung., 25: 978.; Reinking & Wollenweber, 1927, Philipp J. Sci., 32: 206, ic.; Wollenweber, 1931, Z. Parasitenk., 3: 464.; Wollenweber and Reinking, 1935, Die Fusarien, p. 134, ic.; Die Verbreitung der Fusarien in der Natur, p. 38.; Bugnicourt, F., 1939, Encyclopedie mycol., 11: 133, ic.; Wollenweber, 1943, Zbl. Bakt. Abt. II, 106: 110, 186.; Subramanian, C.V., 1952, Proc. Nat. Inst. Sci. India, 18: 581, ic.

Wollenweber, Fus. del. 401-403, 630.

Microconidia present, mostly 1-celled, oval to oblong, and sometimes slightly curved. Macroconidia abundant, up to 4- but mostly 3-septate, dorsiventral, fusiform to falcate, thick-walled, septa distinct, curvature slight in the central part of the conidium, more decided near the apex: apex somewhat rounded; base mamillate. Chlamydospores present, terminal or intercalary, 1-2-celled, globose or pear-shaped; 1-celled 8·8 × 8·8 (8-11 × 8-11), 2-celled 15 × 9·5 (11-19 × 8-12)

Isolated from roots of damped-off seedlings of *Dolichos biflorus* Linn. (Leguminosae), from roots of wilted plants of *Phaseolus radiatus* Linn. (Leguminosae), from roots of wilted plants of *Solanum melongena* Linn. (Solanaceae) and from wilted plants of *Lycopersicon esculentum* Mill. (Solanaceae), collected at the Agricultural Research Institute, Coimbatore; from roots of damped-off seedlings of *Coriandrum sativum* Linn. (Umbelliferae), and from roots of wilted plants of *Cicer arietinum* Linn. (Leguminosae), grown in Udamalpet black cotton soil in pots, University Botany Laboratory, Madras. So far as I am aware, the fungus has not been reported on the above hosts.

The isolate from Dolichos biflorus:

On potato dextrose agar: growth white and loosely fluffy; microconidia scattered or borne in false heads; macroconidia scattered in the aerial mycelium or produced in sporodochia of a bluish colour; chlamydospores mostly terminal.

Measurements of Conidia

0-septate $12 \times 3 \cdot 7$ (8-17 × 2-5)
1-septate $18 \times 4 \cdot 2$ mostly 16-20 × 4·2 (14-24 × 3-5)
2-septate $25 \times 4 \cdot 6$ mostly 21-27 × 4·2-4·9 (19-29 × 4-5)
3-septate $30 \times 4 \cdot 9$ mostly 26-34 × 4·9 (21-39 × 4-6)
4-septate $35 \times 4 \cdot 9$

The isolate from Phaseolus radiatus

On potato dextrose agar: growth adpressed with little aerial mycelium; sporodochia very abundant, greyish blue in colour, coalescing to form a pionnotal layer; chlamydospores mostly terminal, sometimes in chains, occurring in mycelium and in conidia.

Measurements of Conidia

0-septate $13 \times 3 \cdot 8$ mostly 11-15 × 3·3-4·2 (8-15 × 3-5)
1-septate $18 \times 4 \cdot 2$ mostly 14-20 × 4·2 (13-22 × 3-5)
2-septate $25 \times 4 \cdot 9$
3-septate $29 \times 4 \cdot 9$ mostly 28-32 × 4·9 (21-34 × 4-6)

The isolate from Solanum melongena:

On potato dextrose agar: mycelial growth white, compactly fluffy, raised, often cottony; macroconidia produced abundantly in sporodochia of a mm. or less than a mm. in size and of a cream colour, or borne in large groups scattered in the aerial mycelium; conidial chlamydospores particularly abundant in cultures.

Measurements of Conidia

0-septate $13 \times 3 \cdot 8$ mostly 11-15 × 3·3-4·2 (8-15 × 3-5)
1-septate $17 \times 3 \cdot 9$ mostly 14-20 × 3·3-4·2 (13-24 × 3-5)
2-septate $24 \times 4 \cdot 2$ mostly 21-27 × 4·2 (18-29 × 3-5)
3-septate $32 \times 4 \cdot 7$ mostly 28-35 × 4·2-4·9 (21-39 × 4-5)
4-septate $35 \times 4 \cdot 9$ mostly 33-37 × 4·9 (29-39 × 4-6)

The isolate from Lycopersicon esculentum:

On potato dextrose agar: growth white, fluffy, raised, with development of bluish green sporodochia, coalescing to form a slimy pionnotal layer; chlamydospores sometimes in chains, often verrucose.

Measurements of Conidia

0-septate 11 × 3·5 mostly 9-12 × 3·3-4·2 (8-14 × 2-5)
1-septate 17 × 4·1 mostly 13-19 × 3·3-4·2 (11-29 × 3-5)
2-septate 22 × 4·2
3-septate 29 × 4·7 mostly 26-32 × 4·2-4·9 (24-34 × 4-5)

The isolate from Coriandrum sativum:

On potato dextrose agar: growth adpressed with profuse development of sporodochia of a bluish green colour, coalescing to form a pionnotes; chlamydospores smooth or with crenulations.

Measurements of Conidia

0-septate 13 × 3·4 mostly 11-15 × 3·3-4·2 (6-17 × 2-5)
1-septate 19 × 4·3 mostly 16-22 × 4·2 (13-29 × 3-5)
2-septate 22 × 4·5 mostly 19-25 × 4·2-4·9 (18-27 × 4-5)
3-septate 27 × 4·7 mostly 24-30 × 4·2-4·9 (21-35 × 4-5)

The isolate from Cicer arietinum:

On potato dextrose agar: growth slightly fluffy with white aerial mycelium; sporodochia of a bluish or greyish blue colour present, scattered.

Measurements of Conidia

0-septate 10 × 3·5 mostly 9-12 × 3·3-4·2 (8-14 × 3-5)
1-septate 15 × 4·1 mostly 13-17 × 4·2 (11-20 × 3-5)
3-septate 30 × 4·9 mostly 26-34 × 4·9 (24-37 × 4-5)
4-septate 34 × 4·9

F. solani (Mart.) App. et Wr. v. **striatum** (Sherb.) Wr.

Wollenweber, 1931, Z. Parasitenk., 3: 451, 483, ic.; Wollenweber & Reinking, 1935, Die Fusarien, p. 135, ic.; Die Verbreitung der Fusarien in der Natur, p. 38.; Wollenweber, 1943, Zbl. Bakt., Abt. II, 106: 110, 187, ic.; Subramanian, C.V., 1952, Proc. Nat. Inst. Sci. India, 18: 582, ic.

Wollenweber, Fus. del. 406, 1030.

Microconidia present, mostly 1-celled, oval to oblong, scattered in the aerial mycelium or else in false heads. Macroconidia dorsiventral and falcate, with curvature in the middle of the conidium, thick-walled, with clear septa; basal cell somewhat triangular and mamillate or sub-pedicellate, apical cell curved and narrowed into

a rounded apex, septa mostly equidistant; conidial shape almost cylindrical except near the apex where it is slightly broader. Chlamydospores present, terminal or intercalary, 1-2-celled or in chains, globose to pear-shaped when 1-celled; mostly with smooth walls, but sometimes with poorly developed crenulations; 1-celled 9×9 ($8\text{-}10 \times 8\text{-}10$); 2-celled 15×9 ($13\text{-}17 \times 8\text{-}10$).

Isolated from roots of wilted plants of *Solanum melongena* Linn. (Solanaceae), and from roots of wilted plants of *Lycopersicon esculentum* Mill. (Solanaceae), collected at the Agricultural Research Institute, Coimbatore; from roots of wilted plants of *Ananas sativus* Schult. (Bromeliaceae), collected from the Agricultural Research Station, Kovilpatti, Tinnevelly District (Madras State). No so far reported on the above hosts.

The isolate from Solanum melongena:

On potato dextrose agar: growth adpressed with spores forming a brown or light honey coloured pionnotes.

Measurements of Conidia

0-septate $11 \times 3{\cdot}7$ mostly $9\text{-}14 \times 3\text{-}4{\cdot}2$ ($6\text{-}15 \times 3\text{-}5$)
1-septate $18 \times 4{\cdot}2$ mostly $14\text{-}22 \times 4{\cdot}2$ ($11\text{-}24 \times 3\text{-}5$)
2-septate $23 \times 4{\cdot}3$ mostly $21\text{-}25 \times 4{\cdot}2$ ($19\text{-}29 \times 4\text{-}5$)
3-septate $34 \times 4{\cdot}6$ mostly $28\text{-}38 \times 4{\cdot}2\text{-}4{\cdot}9$ ($23\text{-}44 \times 4\text{-}5$)
4-septate $40 \times 4{\cdot}9$ mostly $34\text{-}44 \times 4{\cdot}9$ ($34\text{-}47 \times 4\text{-}6$)
5-septate $43 \times 4{\cdot}9$ mostly $41\text{-}45 \times 4{\cdot}9$ ($39\text{-}47 \times 4\text{-}5$)

The isolate from Lycopersicon esculentum:

On potato dextrose agar: growth velvetty and white with production of conidia scattered or in sporodochia of a pale dull colour.

Measurements of Conidia

0-septate $15 \times 3{\cdot}9$ mostly $11\text{-}17 \times 3{\cdot}3\text{-}4{\cdot}2$ ($9\text{-}20 \times 2\text{-}5$)
1-septate $24 \times 4{\cdot}7$ mostly $21\text{-}27 \times 4{\cdot}2\text{-}4{\cdot}9$ ($18\text{-}30 \times 4\text{-}5$)
2-septate $31 \times 4{\cdot}9$ mostly $28\text{-}34 \times 4{\cdot}9$ ($26\text{-}37 \times 4\text{-}6$)
3-septate $36 \times 4{\cdot}9$ mostly $33\text{-}39 \times 4{\cdot}9$ ($29\text{-}45 \times 4\text{-}5$)

The isolate from Ananas sativus:

On potato dextrose agar: growth adpressed with profuse development of somewhat cream coloured sporodochia and pionnotes.

Measurements of Conidia

0-septate $10 \times 3 \cdot 4$ mostly $9\text{-}12 \times 3 \cdot 3$ (4-14 × 2-5)
1-septate $15 \times 3 \cdot 6$ mostly $13\text{-}19 \times 3 \cdot 3\text{-}4 \cdot 2$ (9-20 × 3-5)
3-septate $34 \times 4 \cdot 9$ mostly $29\text{-}37 \times 4 \cdot 9$ (23-45 × 4-6)
4-septate $40 \times 5 \cdot 0$ mostly $38\text{-}42 \times 4 \cdot 9$ (34-45 × 4-6)

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Some Factors Affecting the Growth of *Rhizoctonia bataticola* in the Soil

BY

A. T. A. Kovoor

University Botany Laboratory, Madras 5.

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ABSTRACT

Rhizoctonia bataticola is capable of growing in unsterilised soil. An increase of soil moisture increases the activity of bacteria that attack the hyphae in the soil.

The addition of sodium nitrate to the soil inhibits the growth of *R. bataticola*, presumably by stimulating antagonistic soil microflora, especially *Actinomyces* sp.

When calcium superphosphate is added growth is comparatively profuse.

*Rhizoctonia bataticola,** which is one of the causal organisms of cotton root rot in the Punjab (Luthra & Vasudeva, 1938) as well as in Southern India, has been found to be capable of leading a naked saprophytic existence in unsterilised soil. In a series of experiments on the behaviour of *R. bataticola*, the effects of certain factors on its growth in the soil were observed.

EXPERIMENTAL

Technique

The technique adopted was a modification of the Rossi-Cholodny slide technique used by Blair (1943) in his investigations on *Rhizoctonia solani*.

Long slides were buried vertically in the soil in tall rectangular soil containers made out of brown kraft paper coated with paraffin. A disc of the fungus growing on an agar-plate was punched out with a cork-borer and this inoculum was placed against the slide just

* The culture used was obtained from cotton plants and has not been observed to produce pycnidia. Hence it has been referred to as *R. bataticola* and not as *Macrophomina phaseoli*.

underneath the surface of the soil in the container. The moisture level of the soil was maintained by daily adjustment after weighing. At the end of the required number of hours the paper containers were carefully unfolded and the slides removed without shearing their surfaces. Th slides were stained with Rose Bengal, Erythrosin (Jensen, 1934) or Crystal Violet.

According to Blair, an examination of the slides under the microscope shows the growth of the hyphae from the inoculum up to the tips of the most advanced ones. It also gives a clear view of any other micro-organisms that may be present; so that if any bacterial attack occurs a vivid picture of disintegrating hyphae could be obtained.

In the case of *R. bataticola*, however, the technique was not so readily applicable, as the hyphae did not adhere very well on to the slide. Perhaps *R. solani* adheres better because it has much finer and flimsier hyphae than *R. bataticola*, whose hyphae have been observed to be thicker and tougher. Though the hyphae could not be traced continuously, the farthest point at which hyphae could be observed was marked and the distance considered as a comparative index of the distance traversed, if not the actual distance itself.

The Effect of Soil Moisture

The water saturation capacity of garden soil was determined by the method of Keen and Raczkowski (1921). In an experiment to determine the rate of growth of a strain of *R. bataticola* isolated from cotton plants, the soil was maintained at three moisture levels —30%, 50% and 80%. At the end of 120 hours the following readings of the distance traversed by the hyphae were taken:-

Moisture level	*Distance traversed*
30%	12·4 cm.
50%	11·6 cm.
80%	7·5 cm.

At a moisture level of 30% there was no bacterial action, though bacteria could be seen clustering round the hyphae. At 50% bacterial attack was perceptible, and in many places the walls of the hyphae were seen to be corroded. The slides that had been left in 80% moisture showed bacterial attack in its highly advanced stages, where very often the hyphae had been completely eaten away, leaving the bacteria and a few

cell-contents to indicate the position once occupied by the hyphae.

The Effect of Sodium Nitrate in the Soil

The addition of sodium nitrate as an inorganic fertiliser is a common agricultural practice. Its effect on the growth of *R. bataticola* was therefore determined. A fertiliser grade of sodium nitrate containing 15·5% of available nitrogen was used for this purpose. The soil was amended with 0·5% of nitrogen (i.e., 3·22 gms. of sodium nitrate in 100 gms. of soil). The salt was powdered in a mortar and mixed with air-dried soil. The slides were buried, inocula placed, and the moisture of the soil adjusted and maintained at 50%.

Slide number	Set (1)	Set (2)	Set (3)
1	0·0 cm.	5·2 cm.	——
2	0·0 cm.	4·0 cm.	3·0 cm.
3	0·0 cm.	4·0 cm.	3·8 cm.
4	0·0 cm.	6·3 cm.	3·5 cm.

In all the slides of Set (1) a large number of colonies of an *Actinomyces* sp. was observed. They were present in Sets (2) and (3) also, but not in such large numbers.

The Effect of Calcium Superphosphate in the Soil

In this experiment the soil was amended with 0·5% of phosphorus in the form of a fertiliser grade of calcium superphosphate which contained 16 gms. of P_2O_5/35 gms. of superphosphate (i.e., 7 gms. of phosphorus/35 gms. of superphosphate. Hence the fertiliser had to be added in proportion of 2·5 gms. of superphosphate to 100 gms. of soil).

As in the previous experiment the soil was maintained at 50% moisture and observations made after 120 hours. It was found that the growth of the fungus was comparatively profuse. It had traversed 12·7 cm. (compare this with 11·6 cm. in plain soil at the same moisture level).

It was observed that the hyphae were practically devoid of bacterial attack. There were, however, numbers of round-bodied bacteria that remained clumped together taking a dark stain with Rose Bengal. These were not seen to attack the hyphae at all. Other rod-shaped and coccoid forms, which normally attack the hyphae, were found to be absent. The absence of soil bacteria was more striking in certain zones where conglomerations of spindle-shaped crystals (believed to be calcium phosphate) were observed.

It was also seen that growth in the half of the slide nearer to the inoculum was not as profuse as that in the distal half.

DISCUSSION

The free and independent growth of *R. bataticola* in unsterilised soil has been recorded for the first time. Blair (1943) has shown that *R. solani* behaves similarly. In this respect *R. bataticola* resembles soil fungi like *Dactylaria* and *Armillaria* and differs from some Fusaria which are quite incapable of growing in unsterilised soil (Subramanian, 1946).

Though the hyphae grow quickly and profusely, they do not exist for long in the soil—they fall a prey to bacterial attack. Thus, the older hyphae get decomposed while the younger hyphal tips keep on growing until, perhaps, they meet with some stubble where they can colonise and produce sclerotia. Its faculty of fairly fast growth, therefore, serves as a method of dispersal and, to a certain extent, makes up for its lack of spores which, in the case of other soil fungi like *Fusarium* are the means of dispersal.

R. bataticola was found to exhibit an optimum growth at a moisture level of 30% of the soil saturation capacity. Growth at 80% was sluggish. This agrees with the findings of Blair (1943) in the case of *R. solani.* He attributes it to the decrease in soil aeration that accompanies a high moisture level. Garrett (1938) has shown that a high moisture level promotes bacterial activity and decomposition of hyphae in *Ophiobolus graminis.* It is quite probable that in the case of *R. bataticola* both these factors are influencing the organism in the soil.

Normally, the addition of nitrogen to the inorganic nutrition of fungi promotes vegetative growth. Perhaps this would be the effect in an agar culture—but when sodium nitrate is added to unsterilised soil the growth of the fungus is retarded and, in some cases, completely inhibited. There is, of course, the possibility of the salt having leached out or of its having been inactivated by adverse base exchanges; in which case growth should have been at least as profuse as that in plain soil. We are left facing the possibility that sodium nitrate either directly inhibits growth or indirectly promotes some other factor that inhibits growth. In this connection it is interesting to note that colonies of a certain *Actinomyces* sp. were most in evidence where no growth was recorded.

An *Actinomyces* sp. has been isolated which exhibits a certain amount of antagonism towards *R. bataticola* in pure culture (Kovoor, unpublished).

The addition of calcium superphosphate seems to have caused a definite increase in growth. The same effect has been observed by Subramanian (1946) with *Fusarium vasinfectum.* He explains it as being due to a direct nutritional effect on the fungus. It is quite possible that in the case of *R. bataticola* also calcium superphosphate has the same beneficial nutritional effect. There are, however, other important observations that have to be accounted for—the hyphae were seen to be devoid of bacterial attack, and in some zones in the vicinity of phosphate crystals, practically no bacteria existed, although in other places there were large clusters of bacteria which did not attack the hyphae. The promotion of growth by calcium superphosphate may be explained by the following: (a) calcium superphosphate has a direct nutritional effect on the fungus; (b) it wipes out bacteria that normally attack the hyphae and makes it possible for the fungus to flourish unhindered; (c) it indirectly promotes growth by acting as a 'negative catalyst' in bacterial action. The first of these possibilities lends itself to the fact that in many slides hyphae were more profuse in the distal half of the slide. Perhaps, in the course of the daily adjustment of moisture, the superphosphate had leached down and hence was exclusively at the disposal of the hyphae in the lower half; or perhaps the initial growth of the hyphae was made at the expense of the nutrition from the inoculum, as observed by Blair (1943) in *R. solani,* and that it was only later on that the hyphae were able to assimilate the phosphate from the surrounding soil.

The inhibitory effect of calcium superphosphate on bacteria that has been observed could be due to the lowered pH of the soil.

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Twins, Parallel Growths, Parting and Extinction Angles in the Pyroxenes of Charnockites From the Type Area of Sir Thomas Holland

BY

N. Leelananda Rao, M.Sc.

Research Fellow, Dept. of Geology and Geophysics
University of Madras, Madras-25

ABSTRACT

The optic axial plane is invariably parallel to the lamellae in orthopyroxenes and perpendicular to the lamellae in clinopyroxenes. The lamellae are parallel to (100) in both. Growths of the two pyroxenes parallel to (100) are also present. The so-called herring-bone twins are really the result of the accidental growing together of two individuals. The composition face is irrational. The inclined extinction angles in orthopyroxenes are normal extinction angles theoretically possible in orthorhombic crystals.

Parting occurs in both the orthopyroxenes and clinopyroxenes of charnockites, collected from cheri Hill, Pallavaram, the type area of Sir Thomas Holland. In discussing the orientations of parting, twinning and parallel growths in these pyroxenes, relatively to the optical ellipsoid, the crystallographic setting for orthopyroxene, as adopted in the European continent, is observed. It is stated in Klockmann's Lehrbuch der Mineralogie (1948), "Bei der Aufstellung der X X stellt man entgegen der Regel in rhombischen system den spitzen prismenwinkel nach vorn (also a > b), im Übereinstimmung mit der Orientierung der monoklinen Augite Zu erhalten." This continental setting has been recommended by Hess and Phillips (1940).

Blocks digrams, Figures 1 and 2 illustrate the orientation of the lamellae as seen in these pyroxenes.

The lamellae are parallel to the optic axial plane in orthopyroxenes and perpendicular to it in clinopyroxenes. The lamellae are parallel to (100) in both. The relationships are indicated in the stereograms, Figures 3 and 4, of two grains. Photographs of these grains are shown in photos 1 and 2. (Plate I).

It has not been possible to determine the optics of the minute second lamellae found in these grains. They are regarded by Hess

as exsolution lamellae of clinopyroxene in orthopyroxene and of orthopyroxene in clinopyroxene. Muthuswami (1953) figures an intergrowth of the two pyroxenes in charnockites, and gives the authority of Hess (1940) for the crystallographic orientation. In

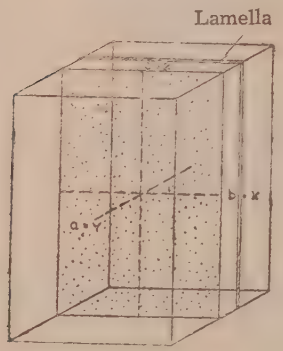


Fig. 1

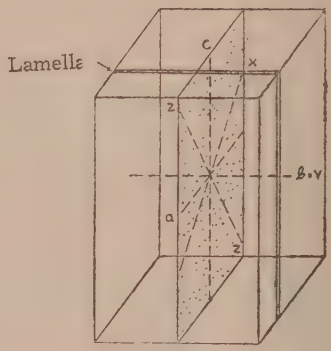


Fig. 2.

Fig. 1. Orientation of op. ax. pl. and lamellae in Hypersthene op. ax. pl = lamellae (100).

Fig. 2. Orientation of op. ax. pl. and lamellae in Diopside op. ax. pl. ⊥ to lamellae (100).

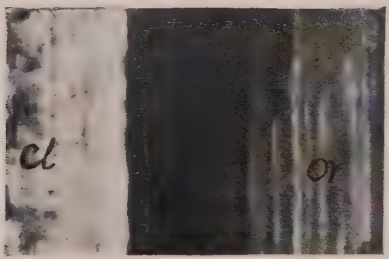
this figure the optic axial plane is shown perpendicular to the lamellae and the lamellae as parallel to (001). From the published work of Hess (1938) it is clear that he regards the lamellae in orthopyroxenes as parallel to the optic axial plane and also parallel either to (100) (continental setting) or to (010) (English and American setting). The orientation of the lamellae as observed in the orthopyroxenes of charnockites accords with the observations of Hess and Phillips.

Besides lamellae of the type noted above, there are also parallel growths of two individuals, or of several individuals together. Photograph 3 (Plate I) is of a parallel growth of one individual of clinopyroxene with another individual of orthopyroxene. Stereogram, figure 6, represents these parallel growths. Block diagram, Fig. 5 represents the parallel growth. Crystallographic axes b of both the pyroxenes coincide with each other; the optic axial planes are perpendicular to each other and the two individuals are united along the face (100), their C crystallographic axes coinciding.

Several twins simulating herring-bone structure were noticed. Photograph 4 (Plate I) is that of orthopyroxene and Photo 5 (Plate I) is of clinopyroxene. The trace of the composition plane

1

2



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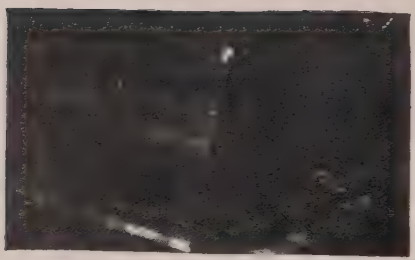

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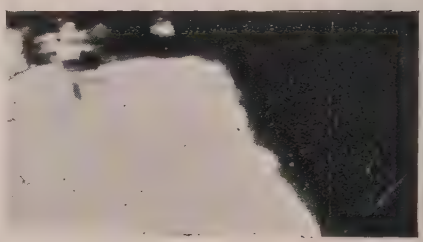

5

Figure 1. Lamellae parallel to (100) in orthopyroxene. The optic axial plane is parallel to the lamellae. The second individual appears as mere streaks of light. × 120 (× Nicols).

Figure 2. Lamellae parallel to (100) in clinopyroxene. The optic axial plane is perpendicular to the lamellae. The second individual appears as streaks of light. × 120. (× Nicols).

Figure 3. Parallel growth of ortho and clinopyroxenes. Or. = orthopyroxenes, Cl = clinopyroxenes. The lamellae in both are parallel to (100). × 120. (× Nicols).

Figure 4. Herring-bone structure of hypersthene. The composition face is irrational. × 120 (× Nicols).

Figure 5. Herring-bone structure of Diopside. The composition face is irrational. × 120 (× Nicols).

is dusted with iron ore, and is not straight. When this plane is plotted in stereographic projection, it occupies an irrational position (pyramidal or domal in character). Stereogram, Figure 8, is of four such grains of diopside, and stereogram 7 is of two grains of hypersthene. The angles measured between the lamellae of each grain were (1) for diopside 100°, 97°, 136°, and 138° and (2) for hypersthene 164°. It is concluded that this herring-bone structure is due not to twinning, but to the accidental growth along an edge of two lamellar individuals.

Muthuswami (1953) again draws attention to the vexed question of inclined extinction in hypersthenes, and quotes the explanation of Hess (1938). He observes inclined extinction up to 20 degrees and says, "Hess (1938) explains this, as due to a composite effect brought about by the lamellae dipping at low angles to the plane of the section." Hess's (1938) full explanation, however, runs thus, "The extinction angles of this orthopyroxene may thus be explained by the composite effect mentioned above, and by the normal extinctions which may be observed in any orthorhombic crystal with prismatic cleavage in sections equivalent in position to a pyramid." Hess therefore does not evaluate the relative importance of the "composite effect" and the "normal extinctions" observed in orthorhombic crystals.

Orthopyroxenes can give extinction angles, on theoretical considerations, up to a maximum of 44° to 46° (in this case symmetrical extinction), according to the trace of the principal sections of the ellipsoid and the cleavages on any section of the mineral. But none of these can be called an extinction angle in the sense that any of the crystallographic axes is inclined to the axes of the optical ellipsoid. Several stereograms were prepared of hypersthene grains (showing lamellae or not) which gave these so-called extinction angles. Stereograms, Figures 9 and 10 are two of those reproduced here. In them are inserted the constructions for extinction according to the Biot—Fresnel law. The observed angles of extinction were 13° and 43° and the theoretical angles of extinction as deduced by Biot—Fresnel law 14° and 43° are not far from these. It is therefore concluded that the extinction angles observed in the orthopyroxenes of charnockites are "the normal extinctions which may be observed in any orthorhombic crystal with prismatic cleavage in sections equivalent in position to a pyramid," (Hess 1938).

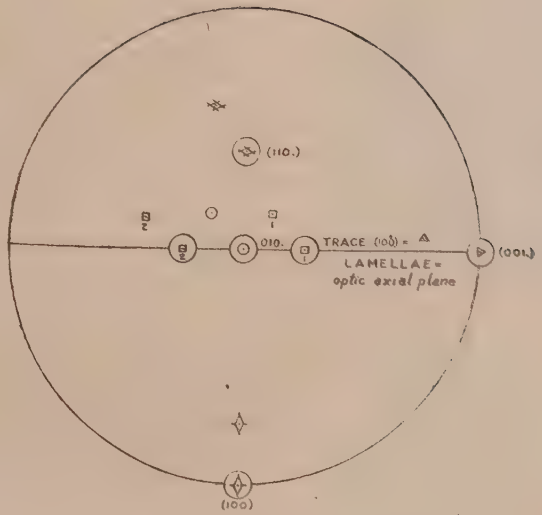

Fig. 3. Stereogram of hypersthene showing lamellae // to the optic axial plane. (continental setting)

= pole (100) = Y
□, ○, ▲, + •

cleavage, optic axis, x, z, and y as observed in the grain.

= transformed poles.

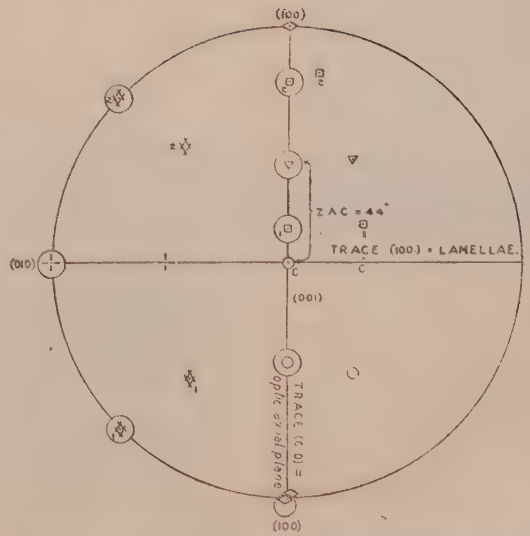

Fig. 4. Stereogram of diopside showing (100) lamellae.

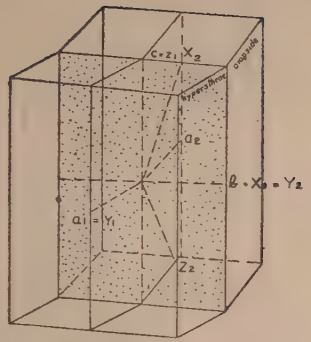

Fig. 5. Parallel growth of Hypersthene and diopside.
dotted plane = (100) of both

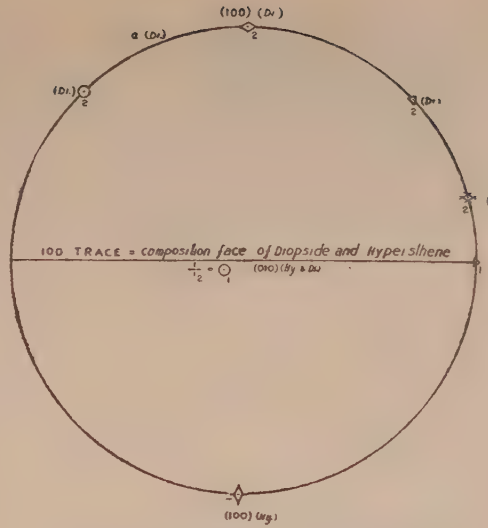

Fig. 6. Stereogram of parallel growth of Hypersthene and Diopside.

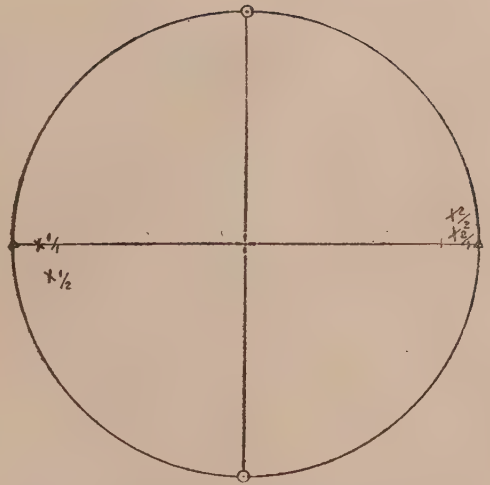

Fig. 7. Stereogram showing the positions of the twin-poles of the so-called herring-bone twins of Hypersthene.
Numerators represent grain numbers.
Denominators represent individuals of each grain.

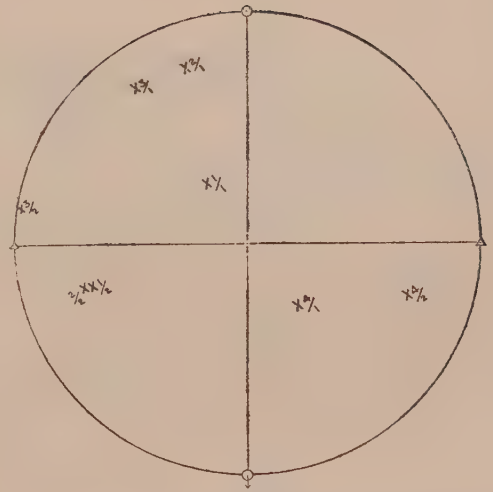

Fig. 8. Stereogram showing the twin poles of the so-called herring-bone twins of Diopside.
Numerators represent grain numbers.
Denominators represent individuals of each grain.

Fig. 9. Stereogram showing inclined extinction of Pyramidal section of Hypersthene.

Fig. 10. Stereogram showing inclined extinction of pyramidal section of Hypersthene.
(100) continental setting = (010) English setting.

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The author avails himself of this opportunity to place on record his deep indebtedness and gratitude to Dr. P. R. J. Naidu for the direction and encouragement he had received all along.

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On the Representation of a Number as the Sum of an Even Number of Squares

BY

K. Ananda Rau

29, *Boag Road, Thyagarayanagar, Madras*

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ABSTRACT

The paper contains proofs based on the theory of elliptic functions of certain identities first enunciated by Ramanujan. These identities, which have occasioned interesting developments in the theory of Dirichlet series, concern the classical problem of the number of representations of an integer as the sum of an even number of squares, the early cases of which were solved by Jacobi. Besides the identities referred to, the method used in this paper is capable of yielding several other identities of interest.

§ 1.

In a paper entitled *On Certain Arithmetical Functions*[1] Ramanujan gave without proof a set of formulae concerning the number of representations of a number as a sum of an even number of squares. These formulae, besides including the classical theorems of Jacobi and the later results of various other authors, go further and give very general identities to cover the case of any even number of squares. The statements of Ramanujan were subsequently proved by Mordell[2] by the application of the theory of modular invariants. Proofs of two particular cases, those concerning eight squares and twenty-four squares were also given by Hardy in one of his lectures[3] on Ramanujan. Hardy's proof is by the method of singular series combined with some of the simpler properties of modular functions.

1. S. Ramanujan, *Collected Papers,* Paper No. 18, paragraphs 24, 25 pages 157-159.

2. L. J. Mordell, *On the representation of members as a sum of 2r squares,* Quarterly Journal of Mathematics, 48 (1920), 93-104. References to earlier work by various authors are given in this paper.

3. G. H. Hardy, *Ramanujan, Twelve Lectures,* Lecture IX. Full references are also given at the end of this Lecture.

The object of this paper is to obtain the results in question from the theory of elliptic functions. It is shown that by choosing four appropriate functions, according as the number of squares is congruent to 0, 2, 4 or 6 to modulus 8, and by obtaining the coefficients in the Taylor series for each function in two different ways we can prove the required identities.

I follow the notation of Tannery and Molk[4] except where specifically stated otherwise. The primitive periods with which the elliptic and allied functions are formed are $2\omega_1$, $2\omega_3$ and their ratio $\tau = \omega_3/\omega_1$ is such that the real part of τ/i is greater than zero; u is a complex variable, $v=u/2\omega_1$, $z=e^{i\pi v}$, $q=e^{i\pi\tau}$, $\vartheta_3(o)=1+2\sum_1^\infty q^{n^2}$ and k, k' are respectively the modulus and the complementary modulus in the sense of Jacobi. I write sometimes ϑ_3 for $\vartheta_3(o)$ of Tannery and Molk; and towards the end of the paper and in the enunciation of the main theorem which follows, it is convenient to write simply ϑ for $\vartheta_3(o)$. I also denote $(kk')^2$ shortly by f.

THEOREM. *Let s denote an integer ≥ 2, and when s is even let $B_{s/2}$ be the numbers of Bernoulli and*

$$\Lambda_s = \frac{2s}{(2^s-1)B_{s/2}} .$$

Further let E_{2n} be the numbers which occur in the Taylor series

$$\sec\ \theta = 1 + \sum_{n=1}^{\infty} \frac{E_{2n}\theta^{2n}}{(2n)!} .$$

Then we have the following identities:

(i) *when* $s \equiv o \pmod 4$

$$\vartheta^{2s} = 1 + \Lambda_s \sum_{p=o}^{\infty} \frac{(2p+1)^{s-1} q^{2p+1}}{1+q^{2p+1}} + \Lambda_s \sum_{p=1}^{\infty} \frac{(2p)^{s-1} q^{2p}}{1-q^{2p}} + \vartheta^{2s} \Pi_s(f);$$

(ii) *when* $s \equiv 2 \pmod 4$

$$\vartheta^{2s} = 1 + \Lambda_s \sum_{p=0}^{\infty} \frac{(2p+1)^{s-1} q^{2p+1}}{1-q^{2p+1}} + \Lambda_s \sum_{p=1}^{\infty} \frac{(2p)^{s-1} q^{2p}}{1+q^{2p}} + \vartheta^{2s} \Pi_s(f);$$

4. J. Tannery and J. Molk, *Eléments de la théorie des functions elliptiques*, 4 volumes. I shall refer to this work shortly as T. M.

(iii) *when* $s \equiv 1 \pmod 4$

$$\vartheta^{2s} = 1 + \frac{2^{s+1}}{E_{s-1}} \sum_{p=1}^{\infty} \frac{p^{s-1} q^p}{1 + q^{2p}} + \frac{4}{E_{s-1}} \sum_{p=o}^{\infty} (-1)^p \frac{(2p+1)^{s-1} q^{2p+1}}{1 - q^{2p+1}} + \vartheta^{2s} \Pi_s(f);$$

(iv) *when* $s \equiv 3 \pmod 4$

$$\vartheta^{2s} = 1 + \frac{2^{s+1}}{E_{s-1}} \sum_{p=1}^{\infty} \frac{p^{s-1} q^p}{1 + q^{2p}} - \frac{4}{E_{s-1}} \sum_{p=o}^{\infty} (-1)^p \frac{(2p+1)^{s-1} q^{2p+1}}{1 - q^{2p+1}} + \vartheta^{2s} \Pi_s(f).$$

In the above the functions $\Pi_s(f)$ *are polynomials in* f *which have the value zero for* $f = o$ *and whose coefficients depend only on* s *and are independent of* ω_1, ω_3, τ. *Further the degree of each of the polynomials is not greater than* $\frac{1}{4}(s-1)$.

§ 2.

The four functions which have to be studied for the proof of the above theorem are related to $\zeta(u)$ and some of the ξ-functions[5], and I shall begin by obtaining suitable expressions for them. We have[6]

$$\xi_{10}(u) = \frac{\sigma_1(u)}{\sigma(u)} = \frac{\vartheta_2(v)}{\vartheta_2(o)} \cdot \frac{\vartheta_1'(o)}{\vartheta_1(v)} \frac{1}{2\omega_1} = \frac{\pi i}{2\omega_1} \cdot \frac{\varrho_1'(1)}{\varrho_2(1)} \cdot \frac{\varrho_2(z)}{\varrho_1(z)}$$

$$\xi_{20}(u) = \frac{\sigma_2(u)}{\sigma(u)} = \frac{\vartheta_3(v)}{\vartheta_3(o)} \cdot \frac{\vartheta_1'(o)}{\vartheta_1(v)} \cdot \frac{1}{2\omega_1} = \frac{\pi i}{2\omega_1} \cdot \frac{\varrho_1'(1)}{\varrho_3(1)} \cdot \frac{\varrho_3(z)}{\varrho_1(z)}$$

$$\xi_{30}(u) = \frac{\sigma_3(u)}{\sigma(u)} = \frac{\vartheta_4(v)}{\vartheta_4(o)} \cdot \frac{\vartheta_1'(o)}{\vartheta_1(v)} \cdot \frac{1}{2\omega_1} = \frac{\pi i}{2\omega_1} \cdot \frac{\varrho_1'(1)}{\varrho_4(1)} \cdot \frac{\varrho_4(z)}{\varrho_1(z)}$$

$$\xi_{21}(u) = \frac{\sigma_2(u)}{\sigma_1(u)} = \frac{\vartheta_3(v)}{\vartheta_3(o)} \cdot \frac{\vartheta_2(o)}{\vartheta_2(v)}$$

$$= \frac{1}{\pi} \cdot \frac{\vartheta_1'(o)}{\vartheta_4(o)} \cdot \pi \cdot \frac{\vartheta_2(o)\vartheta_4(o)}{\vartheta_1'(o)\vartheta_3(o)} \frac{\vartheta_3(v)}{\vartheta_2(v)}$$

$$= \frac{i}{\vartheta_3^2(o)} \cdot \frac{\varrho_1'(1)}{\varrho_4(1)} \frac{\varrho_3(z)}{\varrho_2(z)}$$

5. The properties of the ξ-functions are described in T. M., Vol. II, Chapter IV.

6. For the expression of the σ-functions in terms of the ϑ-functions, see T. M., Vol. II, p. 254. For the expression of the ϑ-functions in terms of the ϱ-functions see T. M., Vol. II, p. 253.

$$\xi_{23}(u) = \frac{\sigma_2(u)}{\sigma_3(u)} = \frac{\vartheta_3(v)}{\vartheta_3(o)} \frac{\vartheta_4(o)}{\vartheta_4(v)}$$

$$= \frac{1}{\pi} \cdot \frac{\vartheta'_1(o)}{\vartheta_2(o)} \cdot \pi \cdot \frac{\vartheta_4(o)\vartheta_2(o)}{\vartheta'_1(o)\vartheta_3(o)} \frac{\vartheta_3(v)}{\vartheta_4(v)}$$

$$= \frac{i}{\vartheta_3^2(o)} \cdot \frac{\varrho_1'(1)}{\varrho_2(1)} \frac{\varrho_3(z)}{\varrho_4(z)} .$$

In the last two identities use is made of the relation[7]

$$\vartheta'_1(o) = \pi\,\vartheta_2(o)\vartheta_3(o)\vartheta_4(o) .$$

On pages 102-104 of Vol. IV of Tannery and Molk's book are given certain infinite series[8] from which we can derive, as particular cases, series for the expressions involving the ϱ-functions in the foregoing identities, and these lead us to resulting infinite series for the ξ-functions. It is convenient to express these latter series in terms of the functions F, G, H defined by

$$F(\theta) = \frac{e^{i\theta}}{1 - e^{2i\theta}}, \qquad G(\theta) = \frac{e^{2i\theta}}{1 - e^{2i\theta}}, \qquad H(\theta) = \frac{e^{i\theta}}{1 + e^{2i\theta}} .$$

Let $\lambda = \pi v$, so that $\lambda = \dfrac{\pi u}{2\omega_1}$, $z = e^{i\lambda}$. Taking $x = 1$ and writing z for y in the infinite series referred to in Tannery and Molk's book we obtain

$$\xi_{10}(u) = \frac{\pi i}{2\omega_1} \frac{\varrho'_1(1)}{\varrho_2(1)} \frac{\varrho_2(z)}{\varrho_1(z)}$$

$$= \frac{\pi i}{2\omega_1} \cdot \frac{z + z^{-1}}{z - z^{-1}} + \frac{\pi i}{\omega_1} \sum_1^\infty (-1)^n \frac{q^{2n}z^{-2}}{1 - z^{-2}q^{2n}}$$

$$- \frac{\pi i}{\omega_1} \sum_1^\infty (-1)^n \frac{q^{2n}z^2}{1 - z^2q^{2n}}$$

$$= \frac{\pi}{2\omega_1} \cot\lambda + \frac{\pi i}{\omega_1} \sum_1^\infty (-1)^n \frac{e^{2i(n\pi\tau - \lambda)}}{1 - e^{2i(n\pi\tau - \lambda)}}$$

$$- \frac{\pi i}{\omega_1} \sum_1^\infty (-1)^n \frac{e^{2i(n\pi\tau + \lambda)}}{1 - e^{2i(n\pi\tau + \lambda)}}$$

7. T. M., Vol. II, p. 28.

8. The relevant identities are the fourth and the last formulae on page 102 in the case of $\xi_{10}(u)$ and $\xi_{23}(u)$ respectively, and the first, second and fourth formulae on page 104 in the case of $\xi_{20}(u)$, $\xi_{21}(u)$ and $\xi_{30}(u)$ respectively.

$$= \frac{\pi}{2\omega_1} \cot \lambda + \frac{\pi i}{\omega_1} \Phi_{10}(\lambda), \qquad .. \quad (1)$$

where $\Phi_{10}(\lambda) = \sum_1^\infty (-1)^n \{G(n\pi\tau - \lambda) - G(n\pi\tau + \lambda)\}$.

Next

$$\xi_{20}(u) = \frac{\pi i}{2\omega_1} \cdot \frac{\varrho'_1(1)}{\varrho_3(1)} \cdot \frac{\varrho_3(z)}{\varrho_1(z)}$$

$$= \frac{\pi i}{2\omega_1} \cdot \frac{2.}{z - z^{-1}} + \frac{\pi i}{\omega_1} \sum_1^\infty (-1)^n \frac{q^n z^{-1}}{1 - z^{-2}q^{2n}}$$

$$- \frac{\pi i}{\omega_1} \sum_1^\infty (-1)^n \frac{q^n z}{1 - z^2 q^{2n}}$$

$$= \frac{\pi}{2\omega_1} \operatorname{cosec} \lambda + \frac{\pi i}{\omega_1} \sum_1^\infty (-1)^n \frac{e^{i(n\pi\tau - \lambda)}}{1 - e^{2i(n\pi\tau - \lambda)}}$$

$$- \frac{\pi i}{\omega_1} \sum_1^\infty (-1)^n \frac{e^{i(n\pi\tau + \lambda)}}{1 - e^{2i(n\pi\tau + \lambda)}}$$

$$= \frac{\pi}{2\omega_1} \operatorname{cosec} \lambda + \frac{\pi i}{\omega_1} \Phi_{20}(\lambda), \qquad .. \quad (2)$$

where $\Phi_{20}(\lambda) = \sum_1^\infty (-1)^n \{F(n\pi\tau - \lambda) - F(n\pi\tau + \lambda)\}$.

Thirdly,

$$\xi_{30}(u) = \frac{\pi i}{2\omega_1} \frac{\varrho'_1(1)}{\varrho_4(1)} \frac{\varrho_4(z)}{\varrho_1(z)}$$

$$= \frac{\pi i}{2\omega_1} \cdot \frac{2}{z - z^{-1}} + \frac{\pi i}{\omega_1} \sum_1^\infty \frac{q^n z^{-1}}{1 - z^{-2}q^{2n}} - \frac{\pi i}{\omega_1} \sum_1^\infty \frac{q^n z}{1 - z^2 q^{2n}}$$

$$= \frac{\pi}{2\omega_1} \operatorname{cosec} \lambda + \frac{\pi i}{\omega_1} \sum_1^\infty \frac{e^{i(n\pi\tau - \lambda)}}{1 - e^{2i(n\pi\tau - \lambda)}}$$

$$- \frac{\pi i}{\omega_1} \sum_1^\infty \frac{e^{i(n\pi\tau + \lambda)}}{1 - e^{2i(n\pi\tau + \lambda)}}$$

$$= \frac{\pi}{2\omega_1} \operatorname{cosec} \lambda + \frac{\pi i}{\omega_1} \Phi_{30}(\lambda), \qquad .. \quad (3)$$

where $\Phi_{30}(\lambda) = \sum_1^\infty \{F(n\pi\tau - \lambda) - F(n\pi\tau + \lambda)\}$.

Fourthly,

$$\xi_{21}(u) = \frac{1}{\vartheta_3^2(o)} \cdot \frac{i\varrho'_1(1)}{\varrho_4(1)} \cdot \frac{\varrho_3(z)}{\varrho_2(z)}$$

$$= \frac{1}{\vartheta_3^2(o)} \cdot \frac{2}{z + z^{-1}} + \frac{2}{\vartheta_3^2(o)} \sum_1^\infty \frac{q^n z^{-1}}{1 + z^{-2}q^{2n}}$$

$$+ \frac{2}{\vartheta_3^2(o)} \sum_1^\infty \frac{q^n z}{1 + z^2 q^{2n}}$$

$$= \frac{\sec\lambda}{\vartheta_3^2(o)} + \frac{2}{\vartheta_3^2(o)} \sum_1^\infty \frac{e^{i(n\pi\tau - \lambda)}}{1 + e^{2i(n\pi\tau - \lambda)}} + \frac{2}{\vartheta_3^2(o)} \sum_1^\infty \frac{e^{i(n\pi\tau + \lambda)}}{1 + e^{2i(n\pi\tau + \lambda)}}$$

$$= \frac{\sec\lambda}{\vartheta_3^2(o)} + \frac{2}{\vartheta_3^2(o)} \Phi_{21}(\lambda), \qquad .. \quad (4)$$

where $\Phi_{21}(\lambda) = \sum_1^\infty \{H(n\pi\tau - \lambda) + H(n\pi\tau + \lambda)\}$.

Fifthly,

$$\xi_{23}(u) = \frac{1}{\vartheta_3^2(o)} \cdot \frac{i\varrho'_1(1)}{\varrho_2(1)} \cdot \frac{\varrho_3(z)}{\varrho_4(z)}$$

$$= \frac{1}{\vartheta_3^2(o)} - \frac{2}{\vartheta_3^2(o)} \sum_1^\infty (-1)^n \frac{q^{2n-1}z^{-2}}{1 - z^{-2}q^{2n-1}}$$

$$- \frac{2}{\vartheta_3^2(o)} \sum_1^\infty (-1)^n \frac{q^{2n-1}z^2}{1 - z^2 q^{2n-1}}$$

$$= \frac{1}{\vartheta_3^2(o)} - \frac{2}{\vartheta_3^2(o)} \cdot \sum_1^\infty (-1)^n \frac{e^{(2n-1)i\pi\tau - 2i\lambda}}{1 - e^{(2n-1)i\pi\tau - 2i\lambda}}$$

$$- \frac{2}{\vartheta_3^2(o)} \sum_1^\infty (-1)^n \frac{e^{(2n-1)i\pi\tau + 2i\lambda}}{1 - e^{(2n-1)i\pi\tau + 2i\lambda}}$$

$$= \frac{1}{\vartheta_3^2(o)} - \frac{2}{\vartheta_3^2(o)} \Phi_{23}(\lambda), \qquad .. \quad (5)$$

where

$$\Phi_{23}(\lambda) = \sum_1^\infty (-1)^n \{G(n\pi\tau - \pi\tau/2 - \lambda) + G(n\pi\tau - \pi\tau/2 + \lambda)\}.$$

Lastly using a formula of Weierstrass[9] with $\zeta(\omega_1) = \eta_1$,

$$\zeta(u) = \frac{\eta_1 u}{\omega_1} + \frac{\pi i}{\omega_1}\left(\frac{z+z^{-1}}{z-z^{-1}} + 2\sum_1^\infty \frac{q^{2n}z^{-2}}{1-z^{-2}q^{2n}} - 2\sum_1^\infty \frac{q^{2n}z^2}{1-z^2q^{2n}}\right)$$

$$= \frac{\eta_1 u}{\omega_1} + \frac{\pi}{2\omega_1}\cot\lambda + \frac{\pi i}{\omega_1}\sum_1^\infty \frac{e^{2i(n\pi\tau-\lambda)}}{1-e^{2i(n\pi\tau-\lambda)}}$$

$$+ \frac{\pi i}{\omega_1}\sum_1^\infty \frac{e^{2i(n\pi\tau+\lambda)}}{1-e^{2i(n\pi\tau+\lambda)}}$$

$$= \frac{\eta_1 u}{\omega_1} + \frac{\pi}{2\omega_1}\cot\lambda + \frac{\pi i}{\omega_1}\Psi(\lambda), \qquad \ldots \quad (6)$$

where $\Psi(\lambda) = \sum_1^\infty \{G(n\pi\tau - \lambda) - G(n\pi\tau + \lambda)\}.$

The four functions of u whose Taylor series in the domain of $u = 0$ have to be considered are $R(u)$, $T(u)$, $V(u)$, $W(u)$ defined as follows:

$$R(u) = \xi_{20}(u) - \zeta(u), \qquad T(u) = \xi_{30}(u) - \xi_{10}(u),$$
$$V(u) = \xi_{23}(u) + \xi_{21}(u), \qquad W(u) = \xi_{23}(u) - \xi_{21}(u).$$

It will be observed that since $\zeta(u)$, $\xi_{10}(u)$, $\xi_{20}(u)$, $\xi_{30}(u)$ have each a pole of the first order at $u = 0$ with residue 1, the functions $R(u)$, $T(u)$ are analytic for $u = 0$, and since $\xi_{21}(u)$, $\xi_{23}(u)$ are analytic for $u = 0$ the same is true of $V(u)$, $W(u)$. Further since $\zeta(u)$, $\xi_{10}(u)$, $\xi_{20}(u)$, $\xi_{30}(u)$ are odd functions, $R(u)$, $T(u)$ are also odd; and since $\xi_{21}(u)$, $\xi_{23}(u)$ are even functions, $V(u)$, $W(u)$ are even.

We proceed to find the mth derivative of $R(u)$, $T(u)$, $V(u)$, $W(u)$ for $u = 0$, the parity of m and the smallest m considered depending on the function we deal with. Let $R^{(m)}(u)$ stand for the mth derivative of $R(u)$ with similar notation for the other functions.

9. H. A. Schwarz, *Formeln und Lehrsätze zum Gebrauche der elliptischen Functionen*, (1893), p. 10, section 8, formula (6). Allowance has to be made for difference in notation.

Using (2) and (6) and replacing $\operatorname{cosec}\lambda - \cot\lambda$ by $\tan\frac{\lambda}{2}$ we get

$$R(u) = \frac{\pi}{2\omega_1}\tan\frac{\lambda}{2} - \frac{\eta_1 u}{\omega_1} + \frac{\pi i}{\omega_1}\Phi_{20}(\lambda) - \frac{\pi i}{\omega_1}\Psi(\lambda).$$

Similarly from (1), (3), (4), (5) we obtain

$$T(u) = \frac{\pi}{2\omega_1}\tan\frac{\lambda}{2} + \frac{\pi i}{\omega_1}\Phi_{30}(\lambda) - \frac{\pi i}{\omega_1}\Phi_{10}(\lambda),$$

$$V(u) = \frac{1+\sec\lambda}{\vartheta_3^2(o)} - \frac{2}{\vartheta_3^2(o)}\Phi_{23}(\lambda) + \frac{2}{\vartheta_3^2(o)}\Phi_{21}(\lambda),$$

$$W(u) = \frac{1-\sec\lambda}{\vartheta_3^2(o)} - \frac{2}{\vartheta_3^2(o)}\Phi_{23}(\lambda) - \frac{2}{\vartheta_3^2(o)}\Phi_{21}(\lambda).$$

Now let m be an odd integer ≥ 3. Remembering that $\lambda = \frac{\pi u}{2\omega_1}$, and writing $\frac{\pi}{2\omega_1} = \triangle$, we have

$$R^{(m)}(u) = \triangle^{m+1}\frac{d^m}{d\lambda^m}\left(\tan\frac{\lambda}{2}\right) + \frac{\pi i}{\omega_1}\triangle^m\Phi^{(m)}{}_{20}(\lambda) - \frac{\pi i}{\omega_1}\triangle^m\Psi^{(m)}(\lambda).$$

If we assume for the moment that it is legitimate to differentiate termwise any number of times the series which define $\Phi_{20}(\lambda)$, $\Psi(\lambda)$, when u lies in a suitably small circle with $u = 0$ as centre, we obtain on such differentiation m times and on putting $u = o$ (and therefore also $\lambda = o$)

$$R^{(m)}(o) = \triangle^{m+1}C_m - 4i\,\triangle^{m+1}\sum_{n=1}^{\infty}(-1)^n F^{(m)}(n\pi\tau) + 4i\,\triangle^{m+1}\sum_{n=1}^{\infty}G^{(m)}(n\pi\tau), \quad \ldots (7)$$

where C_m is the value for $\lambda = o$ of $\frac{d^m}{d\lambda^m}(\tan\frac{\lambda}{2})$.

By similar considerations, if we assume the validity of termwise differentiation any number of times of the series which define $\Phi_{10}(\lambda)$, $\Phi_{30}(\lambda)$, $\Phi_{21}(\lambda)$, $\Phi_{23}(\lambda)$, when u lies in a suitably small circle with $u = o$ as centre, we obtain the following:

If m is an odd integer ≥ 1

$$T^{(m)}(o) = \triangle^{m+1}C_m - 4i\triangle^{m+1}\sum_{n=1}^{\infty} F^{(m)}(n\pi\tau)$$

$$+ 4i\triangle^{m+1}\sum_{n=1}^{\infty}(-1)^n G^{(m)}(n\pi\tau). \quad .. \quad (8)$$

If m is an even integer ≥ 2 and E_m is the value[10] for $\lambda = o$ of $\frac{d^m}{d\lambda^m}(\sec\lambda)$,

$$V^{(m)}(o) = \frac{\triangle^m E_m}{\vartheta_3^2(o)} - \frac{4\triangle^m}{\vartheta_3^2(o)}\sum_{n=1}^{\infty}(-1)^n G^{(m)}(n\pi\tau - \pi\tau/2)$$

$$+ \frac{4\triangle^m}{\vartheta_3^2(o)}\sum_{n=1}^{\infty} H^{(m)}(n\pi\tau). \quad .. \quad (9)$$

Lastly, if m is an even integer ≥ 2

$$W^{(m)}(o) = -\frac{\triangle^m E_m}{\vartheta_3^2(o)} - \frac{4\triangle^m}{\vartheta_3^2(o)}\sum_{n=1}^{\infty}(-1)^n G^{(m)}(n\pi\tau - \pi\tau/2)$$

$$- \frac{4\triangle^m}{\vartheta_3^2(o)}\sum_{n=1}^{\infty} H^{(m)}(n\pi\tau). \quad .. \quad (10)$$

It is easy to establish the validity of the termwise differentiation of the series for the Ψ-function and the Φ-functions. The proofs in the six cases are so similar that it is sufficient to give the details in one case, as the modifications required in the other cases are fairly obvious. Let us take, for example, the series

10. This definition of E_m is in conformity with the definition of $E_{2\nu}$ in the statement of the main theorem at the commencement of this paper.

$$\Phi_{10}(\lambda) = \sum_{1}^{\infty} (-1)^n \{G(n\pi\tau - \lambda) - G(n\pi\tau + \lambda)\}. \quad .. \quad (11)$$

Since the poles of $G(\theta)$ are $r\pi$, where r takes all integer values, positive, negative and zero, it follows that the poles of the terms of the series in (11) can only occur when λ has the values $r\pi + n\pi\tau$, where r takes the values mentioned above and n takes positive and negative integer values but not the value zero. Clearly zero is not a limit point of the poles of the terms, and we can therefore describe with $u = 0$ as centre a circle S in which all the terms of the series (11) are analytic. When the circle S is fixed, there exists a constant $L > 0$ so that for u in S we have $|\cos 2\lambda| < L$, $|\sin 2\lambda| < L$. Further since $|q| < 1$, there is a positive integer N so that for $n > N$ we have

$$2L|q|^{2n} + |q|^{4n} < \tfrac{1}{2}. \quad .. \quad (12)$$

Now consider the series

$$\sum_{n=N+1}^{\infty} (-1)^n \{G(n\pi\tau - \lambda) - G(n\pi\tau + \lambda)\}. \quad .. \quad (13)$$

It is easily seen that[11]

$$|G(n\pi\tau - \lambda) - G(n\pi\tau + \lambda)| = \left| \frac{q^{2n}z^{-2}}{1 - q^{2n}z^{-2}} - \frac{q^{2n}z^2}{1 - q^{2n}z^2} \right|$$

$$= \frac{|q^{2n}(z^{-2} - z^2)|}{|1 - q^{2n}(z^2 + z^{-2}) + q^{4n}|} = \frac{2|q|^{2n}|\sin 2\lambda|}{|1 - 2q^{2n}\cos 2\lambda + q^{4n}|}.$$

If u is in S and $n > N$, we have in virtue of (12)

$$|2q^{2n}\cos 2\lambda - q^{4n}| < 2L|q|^{2n} + |q|^{4n} < \tfrac{1}{2},$$

$$|1 - 2q^{2n}\cos 2\lambda + q^{4n}| \geq 1 - |2q^{2n}\cos 2\lambda - q^{4n}| > \tfrac{1}{2},$$

and therefore (using $|\sin 2\lambda| < L$)

$$|G(n\pi\tau - \lambda) - G(n\pi\tau + \lambda)| < 4L|q|^{2n},$$

from which follows the uniform convergence of the series (13) for u in S. Since all the terms of (11) are analytic in S and since the addition to (13) of the finite sum

$$\sum_{n=1}^{N} (-1)^n \{G(n\pi\tau - \lambda) - G(n\pi\tau + \lambda)\}$$

11. See one of the earlier steps leading to (1) which expresses $\xi_{10}(u)$ in terms of G.

does not affect uniform convergence, it follows that (11) is a series which is uniformly convergent for u in S and whose terms are all analytic in S. By a classical theorem of Weierstrass such a series can be differentiated termwise any number of times for u in S.

In order to obtain the ultimate identities we are aiming at, we have to transform the series like $\Sigma(-1)^n F^{(m)}(n\pi\tau)$ which occur in (7), (8), (9), (10) to provide series in q of the Lambert type. For effecting such transformation we observe that if θ is such that $|e^{i\theta}|<1$ and m is an integer >0, then

$$F(\theta)=\frac{e^{i\theta}}{1-e^{2i\theta}}=\sum_{p=0}^{\infty}e^{(2p+1)i\theta} \qquad F^{(m)}(\theta)=i^m\sum_{p=0}^{\infty}(2p+1)^m e^{(2p+1)i\theta}$$

$$G(\theta)=\frac{e^{2i\theta}}{1-e^{2i\theta}}=\sum_{p=1}^{\infty}e^{2pi\theta} \qquad G^{(m)}(\theta)=i^m\sum_{p=1}^{\infty}(2p)^m e^{2pi\theta}$$

$$H(\theta)=\frac{e^{i\theta}}{1+e^{2i\theta}}=\sum_{p=0}^{\infty}(-1)^p e^{(2p+1)i\theta},$$

$$H^{(m)}(\theta)=i^m\sum_{p=0}^{\infty}(-1)^p(2p+1)^m e^{(2p+1)i\theta}.$$

Since the real part of τ/i is greater than zero, the above equalities hold for $\theta=n\pi\tau$, $\theta=n\pi\tau-\dfrac{\pi\tau}{2}$, n being an integer ≥ 1. We are therefore led to the following:[12]

$$\sum_{n=1}^{\infty}F^{(m)}(n\pi\tau)=i^m\sum_{n=1}^{\infty}\sum_{p=0}^{\infty}(2p+1)^m e^{(2p+1)in\pi\tau}$$

$$=i^m\sum_{p=0}^{\infty}(2p+1)^m\sum_{n=1}^{\infty}q^{(2p+1)n}$$

$$=i^m\sum_{p=0}^{\infty}\frac{(2p+1)^m q^{2p+1}}{1-q^{2p+1}}.$$

$$\sum_{n=1}^{\infty}(-1)^n F^{(m)}(n\pi\tau)=i^m\sum_{n=1}^{\infty}(-1)^n\sum_{p=0}^{\infty}(2p+1)^m e^{(2p+1)in\pi\tau}$$

$$=i^m\sum_{p=0}^{\infty}(2p+1)^m\sum_{n=1}^{\infty}(-1)^n q^{(2p+1)n}$$

$$=-i^m\sum_{p=0}^{\infty}\frac{(2p+1)^m q^{2p+1}}{1+q^{2p+1}}$$

12. The change of order in the summation of the several repeated series is easily justified.

$$\sum_{n=1}^{\infty} G^{(m)}(n\pi\tau) = i^m \sum_{n=1}^{\infty} \sum_{p=1}^{\infty} (2p)^m e^{2pin\pi\tau}$$

$$= i^m \sum_{p=1}^{\infty} (2p)^m \sum_{n=1}^{\infty} q^{2pn}$$

$$= i^m \sum_{p=1}^{\infty} \frac{(2p)^m q^{2p}}{1-q^{2p}}$$

$$\sum_{n=1}^{\infty} (-1)^n G^{(m)}(n\pi\tau) = i^m \sum_{n=1}^{\infty} (-1)^n \sum_{p=1}^{\infty} (2p)^m e^{2pin\pi\tau}$$

$$= i^m \sum_{p=1}^{\infty} (2p)^m \sum_{n=1}^{\infty} (-1)^n q^{2pn}$$

$$= -i^m \sum_{p=1}^{\infty} \frac{(2p)^m q^{2p}}{1+q^{2p}}$$

$$\sum_{n=1}^{\infty} (-1)^n G^{(m)}(n\pi\tau - \pi\tau/2) = i^m \sum_{n=1}^{\infty} (-1)^n \sum_{p=1}^{\infty} (2p)^m e^{pi(2n-1)\pi\tau}$$

$$= i^m \sum_{p=1}^{\infty} (2p)^m \sum_{n=1}^{\infty} (-1)^n q^{p(2n-1)}$$

$$= -(2i)^m \sum_{p=1}^{\infty} \frac{p^m q^p}{1+q^{2p}}$$

$$\sum_{n=1}^{\infty} H^{(m)}(n\pi\tau) = i^m \sum_{n=1}^{\infty} \sum_{p=0}^{\infty} (-1)^p (2p+1)^m e^{(2p+1)in\pi\tau}$$

$$= i^m \sum_{p=0}^{\infty} (-1)^p (2p+1)^m \sum_{n=1}^{\infty} q^{(2p+1)n}$$

$$= i^m \sum_{p=0}^{\infty} \frac{(-1)^p (2p+1)^m q^{2p+1}}{1-q^{2p+1}}.$$

Using these last six formulae in the appropriate places in (7), (8), (9), (10) with the restrictions on m (as to parity and minimum value) in the several cases we get

$$\frac{R^{(m)}(o)}{\triangle^{m+1}} = C_m + 4i^{m+1} \sum_{p=0}^{\infty} \frac{(2p+1)^m q^{2p+1}}{1+q^{2p+1}}$$

$$+ 4i^{m+1} \sum_{p=1}^{\infty} \frac{(2p)^m q^{2p}}{1-q^{2p}} \quad .. \quad (14)$$

$$\frac{T^{(m)}(o)}{\triangle^{m+1}} = C_m - 4i^{m+1} \sum_{p=0}^{\infty} \frac{(2p+1)^m q^{2p+1}}{1-q^{2p+1}}$$

$$- 4i^{m+1} \sum_{p=1}^{\infty} \frac{(2p)^m q^{2p}}{1+q^{2p}} \quad .. \quad (15)$$

$$\frac{V^{(m)}(o)}{\triangle^m} = \frac{E_m}{\vartheta_3^2} + \frac{4}{\vartheta_3^2}(2i)^m \sum_{p=1}^{\infty} \frac{p^m q^p}{1+q^{2p}}$$

$$+ \frac{4}{\vartheta_3^2} i^m \sum_{p=0}^{\infty} (-1)^p \frac{(2p+1)^m q^{2p+1}}{1-q^{2p+1}} \quad .. \quad (16)$$

$$\frac{W^{(m)}(o)}{\triangle^m} = -\frac{E_m}{\vartheta_3^2} + \frac{4}{\vartheta_3^2}(2i)^m \sum_{p=1}^{\infty} \frac{p^m q^p}{1+q^{2p}}$$

$$- \frac{4}{\vartheta_3^2} i^m \sum_{p=0}^{\infty} (-1)^p \frac{(2p+1)^m q^{2p+1}}{1-q^{2p+1}} . \quad .. \quad (17)$$

§ 3.

We proceed now to obtain expressions of a different kind for $R^{(m)}(0)$, $T^{(m)}(0)$, $V^{(m)}(0)$, $W^{(m)}(0)$. Besides these we shall also have to consider for an auxiliary purpose the coefficients in the Laurent series in the domain of $u = 0$ of $J(u) = \xi_{30}(u) + \xi_{10}(u)$. Recalling that $\xi_{02}(u)$, $R(u)$, $T(u)$ are odd functions, that $V(u)$, $W(u)$ are even functions, and observing also that $J(u)$ is an odd function with a simple pole at $u = 0$ with residue 2, we may take these functions as having the following expansions in the domain of $u = 0$:

$$\xi_{02}(u) = \sum_{0}^{\infty} \frac{h_n u^{2n+1}}{(2n+1)!}, \qquad R(u) = \sum_{0}^{\infty} \frac{r_n u^{2n+1}}{(2n+1)!},$$

$$T(u) = \sum_{0}^{\infty} \frac{t_n u^{2n+1}}{(2n+1)!}, \qquad J(u) = \frac{2}{u} + \sum_{0}^{\infty} \frac{j_n u^{2n+1}}{(2n+1)!}$$

$$V(u) = \sum_{0}^{\infty} \frac{v_n u^{2n}}{(2n)!}, \qquad W(u) = \sum_{0}^{\infty} \frac{w_n u^{2n}}{(2n)!}.$$

The coefficients h_n have been investigated in detail in Tannery and Molk's book.[13] They are there denoted by $\sqrt{c}A_o^{(n)}$. For studying the coefficients of the other five series above, I show that the functions represented by those series are connected with $\xi_{02}(u)$ by simple relations which enable us to obtain the required properties of r_n, t_n, j_n, v_n, w_n. It is convenient to omit the variable u and to write simply ξ_{02} for $\xi_{02}(u)$ and so on. We require the following lemma in which accented letters like R′, R″ stand for the derivatives with respect to u, the order of the derivative being denoted by the number of accents.

LEMMA 1. *We have*

$$R''\xi_{02} = 2R' + e_2 \qquad .. \quad (18)$$

$$T'\xi_{02} = T \qquad .. \quad (19)$$

$$J'\xi_{02} = -J \qquad .. \quad (20)$$

$$V\xi'_{02} = J\xi_{02} \qquad .. \quad (21)$$

$$W\xi'_{02} = -T\xi_{02}. \qquad .. \quad (22)$$

To prove these equalities we have to make use of some standard identities; if the suffix numbers, α, β, γ, are all different and are among 1, 2, 3 and $\mathscr{P}$ denotes the Weierstrass elliptic function $\mathscr{P}(u)$, then it is known that[14]

$$\mathscr{P} = e_\alpha + \xi_{\alpha o}^2, \quad \xi'_{\alpha o} = -\xi_{\beta o}\xi_{\gamma o}, \quad \xi'_{o\alpha} = \xi_{\beta\alpha}\xi_{\gamma\alpha},$$
$$\xi_{\alpha o}\xi_{o\alpha} = 1, \quad \xi_{\alpha\beta}\xi_{\beta\alpha} = 1, \quad \xi_{\alpha o}\xi_{o\beta} = \xi_{\alpha\beta}.$$

Now $R = \xi_{20} - \zeta$

$$R' = \xi'_{20} + \mathscr{P} = -\xi_{30}\xi_{10} + e_2 + \xi_{20}^2,$$

13. T. M., Vol. III, pages 64-66 and Vol. IV. pages 90-91, Table XCV.

14. T. M., Vol. II, p. 280, Table LIX and p. 281, Table LXI. As the specific places where each of these standard identities is used in the course of the proof of this lemma are obvious, further individual references are not inserted at the several places.

$$\begin{aligned} R'' &= -\xi'_{30}\xi_{10} - \xi_{30}\xi'_{10} + 2\xi_{20}\xi'_{20}, \\ &= \xi_{10}{}^2\xi_{20} + \xi_{30}{}^2\xi_{20} + 2\xi_{20}\xi'_{20}, \\ R''\xi_{02} &= \xi_{10}{}^2 + \xi_{30}{}^2 + 2\xi'_{20} \\ &= \mathscr{P} - e_1 + \mathscr{P} - e_3 + \mathscr{J}\,2(R' -) \\ &= 2R' + e_2, \end{aligned}$$

which proves (18).

Next,

$$\begin{aligned} T &= \xi_{30} - \xi_{10} \\ T' &= \xi'_{30} - \xi'_{10} = -\xi_{10}\xi_{20} + \xi_{30}\xi_{20} \\ T'\xi_{02} &= -\xi_{10} + \xi_{30} = T, \end{aligned}$$

which proves (19).

Thirdly,

$$\begin{aligned} J &= \xi_{30} + \xi_{10}, \\ J' &= \xi'_{30} + \xi'_{10} = -\xi_{10}\xi_{20} - \xi_{30}\xi_{20}, \\ J'\xi_{02} &= -\xi_{10} - \xi_{30} = -J, \end{aligned}$$

which proves (20).

Fourthly,

$$\begin{aligned} V &= \xi_{23} + \xi_{21} \\ V\xi'_{02} &= (\xi_{23} + \xi_{21})\,\xi_{32}\xi_{12} \\ &= \xi_{12} + \xi_{32} \\ &= \xi_{10}\xi_{02} + \xi_{30}\xi_{02} \\ &= \xi_{02}(\xi_{10} + \xi_{30}) = J\xi_{02}, \end{aligned}$$

which proves (21).

Lastly,

$$\begin{aligned} W &= \xi_{23} - \xi_{21} \\ W\xi'_{02} &= (\xi_{23} - \xi_{21})\,\xi_{32}\xi_{12} \\ &= \xi_{12} - \xi_{32} \\ &= \xi_{10}\xi_{02} - \xi_{30}\xi_{02} \\ &= \xi_{02}(\xi_{10} - \xi_{30}) = -T\xi_{02}, \end{aligned}$$

which proves (22).

In stating the lemmas that follow and in the rest of this paper it will be convenient to write $\triangle^2\vartheta_3^4 = \Theta$, $3e_2 = b$, $(kk')^2 = f$. Further $P_\nu = P_\nu(f)$ will denote a polynomial in f with the following properties: (i) its degree is not greater than ν, (ii) its value is zero for $f = 0$, (iii) its coefficients are independent of ω_1 ω_3, τ. P_ν or $P_\nu(f)$ will not necessarily denote the same polynomial at every occurrence of the symbol.

LEMMA 2. *We have for* $n \geqq 0$

$h_n = \Theta^n(1 + P_{n/2})$ or $b\ \Theta^{n-1}\ (1 + P_{(n-1)/2}\ )$ *according as* n *is even or odd; and in particular* $h_0 = 1$, $h_1 = b$.

From the property that $\xi_{02}(u)$ and similar functions satisfy differential equations of a certain type, Tannery and Molk have obtained power series expansions for such functions. On page 65 of Volume III of their book is given the following formula for the coefficients in the power series:

$$A_r^{(n)} = \sum_{(\gamma)} A_{r,\gamma}^{(n)}\, a^{r+\gamma} b^{n-r-2\gamma} c^\gamma, \qquad \ldots \quad (23)$$

which for suitable values of r, a, b, c gives the expression for h_n. It will be observed from the discussion in Vol. III of that book (pages 64-66) that for the case of $\xi_{02}(u)$ we have to take $r = 0$, $a = (e_2 - e_1)\ (e_2 - e_3)$, $b = 3e_2$, $c = 1$. It is then easily seen that $\sqrt{c}A_o^{(n)}$, which is the same as $A_o^{(n)}$, is our h_n. In (23) with $r = 0$, $A^{(n)}{}_{o,\gamma}$ are purely numerical constants, that is, they are independent of ω_1, ω_3, τ and depend only on γ and n. The index of summation γ runs through $0, 1, 2, \ldots, \frac{n}{2}$ or through $0, 1, 2, \ldots, \frac{n-1}{2}$ according as n is even or odd. Also $A^{(n)}{}_{o,o} = 1$. Taking these into consideration and allowing for change of notation we have from (23) for $n \geqq 2$

$$h_n = b^n + \sum_{\mu=1}^{p} M a^\mu b^{n-2\mu}, \qquad \ldots \quad (24)$$

where p is $n/2$ or $(n-1)/2$ according as n is even or odd, and M denotes here and in all that follows a purely numerical constant not necessarily the same at every occurrence and not depending on ω_1, ω_3, τ. M. will depend only on μ and n or p (whatever meaning p has in the context.).

Tannery and Molk[15] give the values of $A_o^{(n)}$ for the first few values of n from which we infer that $h_o = 1$, $h_1 = b$. In proving the properties of h_n asserted by the present lemma we may therefore consider only values of $n \geq 2$, and so make use of (24). To do so we require in the first instance to express a and b^2 in terms of f and Θ. Since[16]

$$\frac{e_2 - e_3}{e_1 - e_3} = k^2, \quad \frac{e_1 - e_2}{e_1 - e_3} = k'^2, \quad (e_1 - e_3)^2 = (\pi/2\omega_1)^4 \vartheta_3^8 = \Theta^2,$$

we obtain

$$a = (e_2 - e_1)(e_2 - e_3) = -k^2k'^2\Theta^2 = -f\Theta^2,$$

$$b^2 = 9e_2^2 = (e_1 + e_3)^2 + 8e_2^2 = (e_1 - e_3)^2 + 4(e_2^2 + e_2^2 + e_1e_3)$$

$$= (e_1 - e_3)^2 + 4(e_2 - e_1)(e_2 - e_3) = \Theta^2 + 4a = \Theta^2(1 - 4f).$$

Now if n is even, $p = \dfrac{n}{2}$

$$b^n = \{\Theta^2(1 - 4f)\}^p = \Theta^n(1 - 4f)^p = \Theta^n(1 + P_{n/2}),$$

and for $\mu = 1, 2, \ldots, p$

$$a^\mu b^{n-2\mu} = (-1)^\mu f^\mu \Theta^{2\mu} \{\Theta^2(1 - 4f)\}^{p-\mu}$$

$$= (-1)^\mu f^\mu (1 - 4f)^{p-\mu}\Theta^{2p}$$

$$= \Theta^n P_{n/2}$$

Therefore from (24)

$$h_n = \Theta^n(1 + P_{n/2}) + \sum_{\mu=1}^{p} M\Theta^n P_{n/2} = \Theta^n(1 + P_{n/2}).$$

Next, if n is odd, $p = \dfrac{n-1}{2}$,

$$b^n = b.\ b^{n-1} = b\{\Theta^2(1 - 4f)\}^p$$

$$= b\Theta^{n-1}(1 - 4f)^p$$

$$= b\Theta^{n-1}(1 + P_{\frac{n-1}{2}}),$$

15. T. M., Vol. IV, pages 90-91, Table XCV, with $A_o^{(n)} = h_n$, $c = 1$.
16. T. M., Vol. II, pages 28, 29.

and for $\mu = 1, 2, \ldots, p$,

$$a^{\mu}b^{n-2\mu} = (-1)^{\mu} f^{\mu}\Theta^{2\mu}\ b\{\Theta^2(1-4f)\}^{p-\mu}$$
$$= (-1)^{\mu}\ b\Theta^{2p} f^{\mu}(1-4f)^{p-\mu}$$
$$= b\Theta^{n-1}P_{\frac{n-1}{2}} .$$

Therefore from (24)

$$h_n = b\Theta^{n-1}(1+P_{\frac{n-1}{2}}) \quad + \sum_{\mu=1}^{p} Mb\Theta^{n-1}P_{\frac{n-1}{2}}$$
$$= b\Theta^{n-1}(1+P_{\frac{n-1}{2}}) .$$

The proof of the lemma is thus completed.

LEMMA 3. *For* $n \geq 1$ *we have*

$$r_n = b\Theta^n(M + P_{n-2}) \text{ or } \Theta^{n+1}(M + P_{(n-1)/2}),$$

according as n is even or odd.

Now $R(u) = \xi_{20}(u) - \zeta(u)$ and from the following series with the first few known coefficients written[17]

$$\sigma(u) = u - \frac{g_2u^5}{240} - \ldots$$

$$\sigma_2(u) = 1 - \frac{e_2}{2}u^2 + \frac{1}{48}(g_2 - 6e_2^2)u^4 + \ldots$$

$$\zeta(u) = \frac{1}{u} - \frac{g_2u^3}{60} - \ldots ,$$

we get $\xi_{20}(u) = \dfrac{\sigma_2(u)}{\sigma(u)} = \dfrac{1}{u} - \dfrac{e_2u}{2} + \dfrac{1}{40}(g_2 - 5e_2^2)u^3 + \ldots$

$$R(u) = \xi_{20}(u) - \zeta(u) = -\frac{e_2u}{2} + \frac{1}{24}(g_2 - 3e_2^2)u^3 + \ldots$$

Therefore $r_1 = \dfrac{1}{4}(g_2 - 3e_2^2)$

$$= \frac{1}{4}\{2(e_1^2 + e_2^2 + e_3^2) - 3e_2^2\}$$

17. T. M., Vol. II, p. 237, Tables IX, XI.

$$= \frac{1}{4}\{2(e_1^2 + e_3^2) - (e_1 + e_3)^2\}$$

$$= \frac{1}{4}(e_1 - e_3)^2 = \frac{1}{4}\Theta^2.$$

On replacing ξ_{02}, R′, R″ by their Taylor series in the identity $2R' + e_2 = R''\,\xi_{02}$ of Lemma 1, and equating coefficients of u^{2n} we have for $n > 1$,

$$\frac{2r_n}{(2n)!} = \frac{r_1 h_{n-1}}{1!\,(2n-1)!} + \frac{r_2 h_{n-2}}{3!\,(2n-3)!} + \cdots + \frac{r_n h_o}{(2n-1)!\,1!} \qquad \ldots (25)$$

If $h_o, h_1, \ldots, h_{n-1}$ and $r_1, r_2, \ldots, r_{n-1}$ are supposed known, the above equation effectively gives r_n, since the coefficient of r_n in that linear equation is

$$\frac{2}{(2n)!} - \frac{h_o}{(2n-1)!\,1!}$$

and is different from zero for $n > 1$. Solving (25) for r_n we get

$$r_n = \sum_{\mu=1}^{n-1} \mathrm{M} r_\mu h_{n-\mu}. \qquad \ldots (26)$$

The proof of the present lemma is effected by induction using (26).

Suppose we assume the truth fo the lemma for $n = 1, 2, \ldots, p-1$. We shall prove its correctness for $n = p$. There are two cases to be considered, when p is even and when p is odd.

Suppose first p is even. From (26)

$$r_p = \sum_{\mu=1}^{p-1} \mathrm{M} r_\mu h_{p-\mu}. \qquad (27)$$

When μ is odd, $p - \mu$ will also be odd; and therefore by our assumption (since $1 \leq \mu \leq p-1$)

$$r_\mu = \Theta^{\mu+1}(\mathrm{M} + \underset{2}{\mathrm{P}_{\mu-1}}),$$

and by Lemma 2

$$h_{p-\mu} = b\Theta^{p-\mu-1}(1 + \underset{2}{\mathrm{P}_{p-\mu-1}}).$$

Therefore observing that $(M + P_{\nu})(M + P_{\nu'}) = M + P_{\nu+\nu'}$ we see that

$$r_\mu h_{p-\mu} = b\Theta^p (M + P_{\frac{p-2}{2}}).$$

On the other hand, when μ is even, $p - \mu$ will also be even; and in that case by our assumption

$$r_\mu = b\Theta^\mu (M + P_{\frac{\mu-2}{2}}),$$

and by Lemma 2

$$h_{p-\mu} = \Theta^{p-\mu} (1 + P_{\frac{p-\mu}{2}}),$$

and so

$$r_\mu h_{p-\mu} = b\Theta^p (M + P_{\frac{p-2}{2}}).$$

Therefore when p is even every term $Mr_\mu h_{p-\mu}$ in the sum in (27) is of the form $b\Theta^p (M + P_{\frac{p-2}{2}})$, and so r_p is also of the same form.

Hence the lemma is true for $n = p$.

We next consider the case when p is odd. As before r_p is given by (27). When μ is odd, $p - \mu$ will be even; therefore by our assumption

$$r_\mu = \Theta^{\mu+1} (M + P_{\frac{\mu-1}{2}}),$$

and by Lemma 2

$$h_{p-\mu} = \Theta^{p-\mu} (1 + P_{\frac{p-\mu}{2}}),$$

and so $$r_\mu h_{p-\mu} = \Theta^{p+1} (M + P_{\frac{p-1}{2}}).$$

On the other hand when μ is even, $p - \mu$ will be odd; therefore by our assumption

$$r_\mu = b\Theta^\mu (M + P_{\frac{\mu-2}{2}}),$$

and by Lemma 2

$$h_{p-\mu} = b\Theta^{p-\mu-1}(1 + P_{\frac{p-\mu-1}{2}}),$$

and therefore, recalling that $b^2 = \Theta^2(1 - 4f)$ we get

$$r_\mu h_{p-\mu} = \Theta^{p+1}(M + P_{\frac{p-1}{2}}).$$

Hence when p is odd every term $Mr_\mu h_{p-\mu}$ in the sum in (27) is of the form $\Theta^{p+1}(M + P_{\frac{p-1}{2}})$, and so r_p is also of the same form.

Hence the lemma is true for $n = p$.

As we have seen that $r_1 = \frac{1}{4}\Theta^2$ and so verified the correctness of the lemma for $n = 1$, the induction is complete and the lemma is proved.

The coefficients t_n, j_n, v_n, w_n have also properties similar to those of r_n and can be proved to have forms resembling the ones stated in Lemma 3 for r_n. The proofs in these fresh cases are also by induction and are so similar to the proof of Lemma 3 that I have not considered it necessary to give all the details. I shall briefly indicate in each of these new cases the formulae analogous to (25) and (26) which provide the basis for the induction, and it will be easily seen that the arguments used in the proof of Lemma 3 have only to be modified in an obvious manner to suit each of the new cases. The results needed are collected in the following lemma.

LEMMA 4. *We have* $t_0 = \frac{\Theta}{2}$, $j_0 = \frac{b}{6}$, $v_0 = 2$, $w_0 = 0$.

Further for $n \geq 1$ *we have*

(i) $t_n = \Theta^{n+1}(M + P_{\frac{n}{2}})$ *or* $b\Theta^n(M + P_{\frac{n-1}{2}})$ *according as* n *is even or odd.*

(ii) $j_n = b\Theta^n(M + P_{\frac{n}{2}})$ *or* $\Theta^{n+1}(M + P_{\frac{n+1}{2}})$ *according as* n *is even or odd.*

(iii) $v_n = \Theta^n(\mathrm{M} + \mathrm{P}_{\frac{n}{2}})$ *or* $\mathrm{b}, \Theta^{n-1}(\mathrm{M} + \mathrm{P}_{\frac{n-1}{2}})$ *according as* n *is even or odd.*

(iv) $w_n = \mathrm{b}\Theta^{n-1}(\mathrm{M} + \mathrm{P}_{\frac{n-2}{2}})$ *or* $\Theta^n(\mathrm{M} + \mathrm{P}_{\frac{n-1}{2}})$ *according as* n *is even or odd.*

To prove the result of the lemma for t_n we observe first that in the domain of $u = 0$[18]

$$\mathrm{T} = \xi_{30} - \xi_{10} = \left(\frac{1}{u} - \frac{e_3 u}{2} + \cdots\right) - \left(\frac{1}{u} - \frac{e_1 u}{2} + \cdots\right)$$

$$= \frac{e_1 - e_3}{2} u + \cdots$$

which shows that

$$t_0 = \frac{1}{2}(e_1 - e_3) = \tfrac{1}{2}\Theta. \qquad (28)$$

Next we write the Taylor series for T, T′, ξ_{02} in the identity $\mathrm{T} = \mathrm{T}'\xi_{02}$ of Lemma 1 and equate the coefficients of u^3; using (28) and $h_0 = 1$, $h_1 = b$ we get $t_1 = -\frac{1}{4} b\Theta$. Further equating the coefficients of u^{2n+1} we obtain[19] for $n \geq 1$

$$\frac{t_n}{(2n+1)!} = \sum_{\mu=0}^{n} \frac{t_\mu h_{n-\mu}}{(2\mu)!\,(2n-2\mu+1)!}, \qquad (29)$$

which leads to

$$t_n = \sum_{\mu=0}^{n-1} \mathrm{M} t_\mu h_{n-\mu}. \qquad (30)$$

This relation forms the basis of the induction for the proof of (i) of the present lemma. The value of t_1 found above provides for the completion of the induction.

18. The series for ξ_{30}, ξ_{10} are easily derived from the Taylor series for $\sigma(u)$, $\sigma_2(u)$, $\sigma_1(u)$ in the domain of $u = 0$ given on p. 237, Tables IX, XI in T. M., Vol. II.

19. In the formula (29) and elsewhere 0! is, as usual, to be understood to denote 1.

To prove the result for j_n we observe first that

$$J = \xi_{30} + \xi_{10} = \left(\frac{1}{u} - \frac{e_3 u}{2} + \dots\right) + \left(\frac{1}{u} - \frac{e_1 u}{2} + \dots\right)$$

$$= \frac{2}{u} + \frac{e_2 u}{2} + \dots$$

from which it follows that

$$j_0 = \frac{e_2}{2} = \frac{b}{6}. \qquad \dots (31)$$

Next we write the Laurent series for J, J′ and the Taylor series for ξ_{02} in the identity $J = -J'\xi_{02}$ of Lemma 1 and equate the coefficients of u^3; using (31) and[20] $h_0 = 1$, $h_1 = b$, $h_2 = \Theta^2(1 - 16f)$ we get $j_1 = \Theta^2\left(\frac{5}{144} - \frac{8}{9}f\right)$. Further equating the coefficients of u^{2n+1} we obtain for $n \geq 1$

$$\frac{j_n}{(2n+1)!} = \frac{2h_{n+1}}{(2n+3)!} - \sum_{\mu=0}^{n} \frac{j_\mu h_{n-\mu}}{(2\mu)!\,(2n-2\mu+1)!} \qquad \dots (32)$$

which leads to

$$j_n = Mh_{n+1} + \sum_{\mu=0}^{n-1} Mj_\mu h_{n-\mu}. \qquad \dots (33)$$

This relation forms the basis of the induction for the proof of (ii) of the present lemma. The value of j_1 found above provides for the completion of the induction.

Thirdly, to prove the result for v_n we observe that since $\xi_{21}(o) = 1$, $\xi_{23}(o) = 1$ we have $v_0 = 2$; and writing the Taylor series for V, ξ_{02}, ξ'_{02} and the Laurent series for J in the identity $V\xi'_{02} = J\xi_{02}$ of Lemma 1, and equating the coefficients of u^2 we get $v_1 = -b$. Further on equating the coefficients of u^{2n} we get for $n \geq 1$

$$\sum_{\mu=0}^{n} \frac{v_\mu h_{n-\mu}}{(2\mu)!\,(2n-2\mu)!} = \frac{2h_n}{(2n+1)!}$$

$$+ \sum_{\mu=0}^{n-1} \frac{j_\mu h_{n-\mu-1}}{(2\mu+1)!\,(2n-2\mu-1)!}, \qquad \dots (34)$$

20. T. M., Vol. IV, pages 90, 91, Table XCV with $A_0(n) = h_n$, $c = 1$, $a = -f\Theta^2$, $b^2 = \Theta^2(1 - 4f)$ as proved earlier.

which leads to

$$v_n = Mh_n + \sum_{\mu=0}^{n-1} Mv_\mu h_{n-\mu} + \sum_{\mu=0}^{n-1} Mj_\mu h_{n-\mu-1}. \quad .. \quad (35)$$

This relation forms the basis of the induction for the proof of (iii) of the present lemma. In the induction we have to use not only Lemma 2 but also the value $j_o = \frac{b}{6}$ and the result (ii) of the present lemma. The value $v_1 = -b$ found above provides for the the completion of the induction.

Lastly to prove the result for w_n we observe that in the domain of $u = 0$ we have for $\alpha = 1, 2, 3$ the Taylor series[21]

$$\sigma_\alpha(u) = 1 - \frac{e_\alpha}{2} u^2 + \ldots \quad .. \quad (36)$$

from which we derive

$$\xi_{21}(u) = \frac{\sigma_2(u)}{\sigma_1(u)} = 1 + \frac{e_1 - e_2}{2} u^2 + \ldots$$

$$\xi_{23}(u) = \frac{\sigma_2(u)}{\sigma_3(u)} = 1 + \frac{e_3 - e_2}{2} u^2 + \ldots ,$$

and so it follows that $w_o = 1-1 = 0$, $w_1 = (e_3 - e_2) - (e_1 - e_2) = -\Theta$. Further writing the Taylor series for W, T, ξ_{02}, ξ'_{02} in the identity $W\xi'_{02} = -T\xi_{02}$ of Lemma 1 and equating the coefficients of u^{2n} we get for $n \geq 1$

$$\sum_{\mu=0}^{n} \frac{w_\mu h_{n-\mu}}{(2\mu)!\,(2n-2\mu)!} = \sum_{\mu=0}^{n-1} \frac{t_\mu h_{n-\mu-1}}{(2\mu+1)!\,(2n-2\mu-1)!}, \quad .. \quad (37)$$

which leads to

$$w_n = \sum_{\mu=0}^{n-1} Mw_\mu h_{n-\mu} + \sum_{\mu=0}^{n-1} Mt_\mu h_{n-\mu-1}. \quad (38)$$

21. T. M., Vol. II, p. 237, Table XI.

This relation forms the basis of the induction for the proof of (iv) of the present lemma. In the induction we have to use not only Lemma 2 but also the value $t_o = \frac{1}{2}\Theta$ and the result (i) of the present lemma. The value $w_1 = -\Theta$ found above provides for the completion of the induction.

§ 4

We are now in a position to prove the identities quoted in the main theorem at the commencement of this paper. For this, it is only necessary to identify $\mathrm{R}^{(m)}(0)$, $\mathrm{T}^{(m)}(0)$, $\mathrm{V}^{(m)}(0)$, $\mathrm{W}^{(m)}(0)$ with r_n, t_n, v_n, w_n respectively, the index n being suitably related to m. Before we consider the general cases, it is of interest to deal with three particular cases which give the theorems of Jacobi. For the proofs of these particular cases we do not require Lemmas 1 and 2 nor the general forms of r_n, t_n, v_n, w_n given by Lemmas 3 and 4. We require only the equalities $r_1 = \frac{1}{4}\Theta^2$, $t_o = \frac{1}{2}\Theta$, $w_1 = -\Theta$ all of which can be obtained, as we have seen, directly from the first few known or easily calculated coefficients in the Laurent series for ζ, ξ_{10}, ξ_{20}, ξ_{30} and in the Taylor series for ξ_{21}, ξ_{23}.

Since $\mathrm{R}^{(3)}(o) = r_1$, $\mathrm{C}_3 = \frac{1}{4}$, $r_1 = \frac{1}{4}\Theta^2 = \frac{1}{4}\triangle^4\vartheta^8$ we obtain on using (14) with $m = 3$

$$\vartheta^8 = \frac{4r_1}{\triangle^4} = \frac{4\mathrm{R}^{(3)}(o)}{\triangle^4} = 1 + 16\sum_{p=0}^{\infty}\frac{(2p+1)^3q^{2p+1}}{1+q^{2p+1}} + 16\sum_{p=1}^{\infty}\frac{(2p)^3q^{2p}}{1-q^{2p}}$$

which is Jacobi's identity for the case of eight squares.

Since $\mathrm{T}'(o) = t_o$, $\mathrm{C}_1 = \frac{1}{2}$, $t_o = \frac{1}{2}\Theta = \frac{1}{2}\triangle^2\vartheta^4$, we get on applying (15) with $m = 1$

$$\vartheta^4 = \frac{2t_o}{\triangle^2} = \frac{2T'(o)}{\triangle^2} = 1 + 8 \sum_{p=0}^{\infty} \frac{(2p+1)q^{2p+1}}{1-q^{2p+1}} + 8 \sum_{p=1}^{\infty} \frac{(2p)q^{2p}}{1+q^{2p}},$$

which is Jacobi's identity for the case of four squares.

Next since $W''(o) = w_1$, $E_2 = 1$, $w_1 = -\Theta = -\triangle^2\vartheta^4$, we get on applying (17) with $m = 2$

$$\vartheta^6 = -\frac{w_1\vartheta^2}{\triangle^2} = -\frac{W''(o)\,\vartheta^2}{\triangle^2} = 1 + 16 \sum_{p=1}^{\infty} \frac{p^2q^p}{1+q^{2p}} - 4 \sum_{p=0}^{\infty} (-1)^p \frac{(2p+1)^2 q^{2p+1}}{1-q^{2p+1}},$$

which is Jacobi's identity for the case of six squares.

We now proceed to consider the general case. Let s denote an integer ≥ 2. We take $2s$ as the number of squares in question. There are four alternatives to be considered.

First suppose $s \equiv 0 \pmod 4$. Let $m = 2n+1 = s-1$, so that m and n are odd, $m \geq 3$, $2s = 4n+4$, $\frac{1}{2}(n-1) = \frac{1}{4}(s-4)$. It is easy to verify that

$$C_m = \frac{2(2^s - 1)B_{s/2}}{s} = \frac{4}{\Lambda_s}. \qquad .. \quad (39)$$

$R^{(m)}(0) = r_n$. Therefore applying Lemma 3 for the case n odd we get

$$\frac{R^{(m)}(0)}{\triangle^{m+1}} = \frac{r_n}{\triangle^{m+1}} = \frac{\Theta^{n+1}(M + P_{\frac{n-1}{2}})}{\triangle^{2n+2}}$$

$$= \vartheta^{4n+4}(M + P_{\frac{n-1}{2}}) = \vartheta^{2s}(M + P_{\frac{s-4}{4}}). \qquad .. \quad (40)$$

In the above, M is an undetermined constant independent of τ and therefore also of q. To find M we observe that when $q \to 0$, $\vartheta \to 1$, $k \to 0$, $k' \to 1$, $f \to 0$, $P_{\frac{s-4}{4}} \to 0$. Therefore[22] letting $q \to 0$ in (40)

22. We may not actually put $q = 0$ to find M, as in all the preceding analysis it is assumed that $2\omega_1$, $2\omega_3$ are finite and different from zero, which implies that q is not zero.

we get $\dfrac{R^{(m)}(0)}{\triangle^{m+1}} \to M$. But from (14) $\dfrac{R^{(m)}(0)}{\triangle^{m+1}} \to C_m$ when $q \to 0$. Therefore $M = C_m$. Also $i^{m+1} = 1$. Hence equating the values of $R^{(m)}(0)$ given by (14) and (40), and using (39) we obtain after a slight rearrangement

$$\vartheta^{2s} = 1 + \Lambda_s \sum_{p=0}^{\infty} \frac{(2p+1)^{s-1} q^{2p+1}}{1+q^{2p+1}} + \Lambda_s \sum_{p=1}^{\infty} \frac{(2p)^{s-1} q^{2p}}{1-q^{2p}} + \vartheta^{2s} P_{\frac{s-4}{4}}$$

which is the identity (i) of the main theorem stated at the commencement of this paper.

Next suppose $s \equiv 2 \pmod 4$. Let $m = 2n+1 = s-1$, so that m is odd, n is even, $2s = 4n+4$, $\dfrac{n}{2} = \dfrac{1}{4}(s-2)$. Clearly $T^{(m)}(o) = t_n$. Therefore applying the result (i) of Lemma 4 for the case n even we get

$$\frac{T^{(m)}(o)}{\triangle^{m+1}} = \frac{t_n}{\triangle^{m+1}} = \frac{\Theta^{n+1}(M + P_{n/2})}{\triangle^{2n+2}}$$

$$= \vartheta^{4n+4}(M + P_{\frac{n}{2}}) = \vartheta^{2s}(M + P_{\frac{s-2}{4}}). \qquad .. \quad (41)$$

By letting $q \to 0$ in (41) and in (15) and comparing the limits we find as in the previous case that the M in (41) equals C_m. Further (39) holds in this case also and $i^{m+1} = -1$. Hence equating the values of $T^{(m)}(o)$ given by (41) and (15) we get

$$\vartheta^{2s} = 1 + \Lambda_s \sum_{p=0}^{\infty} \frac{(2p+1)^{s-1} q^{2p+1}}{1-q^{2p+1}} + \Lambda_s \sum_{p=1}^{\infty} \frac{(2p)^{s-1} q^{2p}}{1+q^{2p}} + \vartheta^{2s} P_{\frac{s-2}{4}},$$

which is the identity (ii) of the main theorem.

Thirdly suppose $s \equiv 1 \pmod 4$. Let $m = 2n = s-1$, so that m and n are even, $2s = 4n+2$, $\dfrac{n}{2} = \dfrac{1}{4}(s-1)$. Clearly $V^{(m)}(o) = v_n$. Therefore applying the result (iii) of Lemma 4 for the case n even we get

$$\frac{V^{(m)}(o)}{\triangle^m}\vartheta^2 = \frac{v_n \vartheta^2}{\triangle^m} = \frac{\Theta^n(M + P_{n/2})\vartheta^2}{\triangle^{2n}}$$

$$= \vartheta^{4n+2}(M + P_{\frac{n}{2}}) = \vartheta^{2s}(M + P_{\frac{s-1}{4}}). \qquad .. \quad (42)$$

By letting $q \to 0$ in (42) and in (16) and comparing the limits we find that the M in (42) equals E_m or E_{s-1}. Also $i^m = 1$. Hence equating the values of $V^{(m)}(0)$ given by (42) and (16) we get

$$\vartheta^{2s} = 1 + \frac{2^{s+1}}{E_{s-1}} \sum_{p=1}^{\infty} \frac{p^{s-1}q^p}{1+q^{2p}}$$

$$+ \frac{4}{E_{s-1}} \sum_{p=0}^{\infty} (-1)^p \frac{(2p+1)^{s-1}q^{2p+1}}{1-q^{2p+1}} + \vartheta^{2s} P_{\frac{s-1}{4}}$$

which is identity (iii) of the main theorem.

Lastly suppose $s \equiv 3 \pmod 4$. Let $m = 2n = s-1$, so that m is even, n is odd, $2s = 4n+2$, $\frac{1}{2}(n-1) = \frac{1}{4}(s-3)$. Clearly $W^{(m)}(o) = w_n$. Therefore applying the result (iv) of Lemma 4 for the case n odd we get

$$\frac{W^{(m)}(o)}{\triangle^m} \cdot \vartheta^2 = \frac{w_n \vartheta^2}{\triangle^m} = \frac{\Theta^n (M + P_{(n-1)/2}) \vartheta^2}{\triangle^{2n}}$$

$$= \vartheta^{4n+2}(M + P_{\frac{n-1}{2}}) = \vartheta^{2s}(M + P_{\frac{s-3}{4}}) \quad \ldots \quad (43)$$

By letting $q \to 0$ in (43) and in (17) and comparing the limits we find that the M in (43) equals E_m or E_{s-1}. Also $i^m = 1$. Hence equating the values of $W^{(m)}(o)$ given by (43) and (17) we get

$$\vartheta^{2s} = 1 + \frac{2^{s+1}}{E_{s-1}} \sum_{p=1}^{\infty} \frac{p^{s-1}q^p}{1+q^{2p}}$$

$$- \frac{4}{E_{s-1}} \sum_{p=0}^{\infty} (-1)^p \frac{(2p+1)^{s-1}q^{2p+1}}{1-q^{2p+1}} + \vartheta^{2s} P_{\frac{s-3}{4}}$$

which being identity (iv) of the main theorem completes the proof of that theorem.

It may be observed that Jacobi's identity for the case of two squares, though excluded from the previous discussion for formal reasons, can be obtained quite easily by considering the function $V(u)$ as may be expected, or even more simply by considering $\xi_{21}(u)$ or $\xi_{23}(u)$ — the functions whose sum is $V(u)$. For example, since $\xi_{21}(o) = 1$, we get by putting $u = 0$ (and therefore also $\lambda = 0$) in (4),

$$\vartheta^2 = 1 + 2\,\Phi_{21}(o) = 1 + 4 \sum_{n=1}^{\infty} H(n\pi\tau)$$

$$= 1 + 4 \sum_{n=1}^{\infty} \frac{e^{in\pi\tau}}{1 + e^{2in\pi\tau}} = 1 + 4 \sum_{n=1}^{\infty} \frac{q^n}{1 + q^{2n}}. \qquad .. \quad (44)$$

If we use the series (5) for $\xi_{23}(u)$ we can similarly obtain

$$\vartheta^2 = 1 + 4 \sum_{n=0}^{\infty} (-1)^n \frac{q^{2n+1}}{1 - q^{2n+1}}. \qquad .. \quad (45)$$

Jacobi's identity for the case of two squares is in the alternative forms (44) or (45). It is well known that the equality of the two series in (44) and (45) can be proved by the elementary theory of series.

Besides the identities whose proof has been the main purpose of this paper, other identities of interest can be obtained from the results proved here. We used only part of the conclusions of Lemmas 3 and 4, namely those when n had one or other of the parities—n odd in the case of r_n, w_n, and n even in the case of t_n, v_n. The use of the other half of the Lemmas 3 and 4 leads to identities which are not without interest. Further the method adopted in this paper may be applied with suitable modifications to other functions besides R, T, V, W so as to arrive at various identities. Besides the ζ-functon and the five ξ-functions dealt with here, there are other functions including the remaining seven ξ-functions which are capable of providing transformations leading to identities. These and related matters I hope to be able to consider on a future occasion.

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Ferric Azide Ion-pair As a Photo Sensitizer in the Polymerization of Vinyl Compounds in Aqueous Solution

BY

M. SANTHAPPA

Department of Physical Chemistry, Madras University, Madras-25

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ABSTRACT

In the introductory part previous work leading to the present work has been briefly traced and the terms "electron-transfer" "ion-pair", etc., have been explained. In the experimental part, the methods of calculating the concentration and the fraction of light absorbed by the ion-pairs have been indicated. Experimental results for (a) variation of rate of ferrous ion production, (b) rate of monomer disappearance and (c) chain length of polymer with (i) light absorption fraction, (ii) intensity of light, (iii) concentration of the monomer, (iv) accumulated or initially added ferrous ion and (v) quantum yields for ferrous ion production and monomer disappearance are given. In the discussion part expressions for various possibilities of 'initiation' and 'termination' of polymerization have been derived and experimental results have been examined in the light of these possibilities. Certain differences in the reactions of azide radicals on the one hand and the hydroxyl or halide radicals on the other have been pointed out.

I. INTRODUCTION

Ion Pairs

Rabinowitch and Stockmayer (1942) have made extensive investigations in the chemistry of ferric 'association complexes' or 'ion-pair complexes' in which the cations and the anions like hydroxyl or halide ions are held together by bonding electrons which give dipole character to the complexes. The absorption spectrum of such a complex is associated with (a) the 'excitation' of the non-bonding electron within the atom in the anion or cation and then (b) 'transfer' of the excited electron to the atom in the cation or anion respectively while the electrons binding

the anion and cation of the complex are supposed to be not affected by light absorption. The term 'Electron transfer spectra' has been used to describe the spectra of such complexes. On the other hand the term 'Electronic spectra' is associated with excitation of either the bonding electrons of the complex or non-bonding electrons within the individual ions of the complex without the transfer of the excited electron from one to the other ion ever occurring. Complexes exhibiting purely electronic spectra have come to be called 'true' or 'atomic' complexes. Electronic spectra are altered but little by variation in concentrations of the individual ions of the complex while new absorption bands appear by variation in concentration of the individual associating ions of the 'ion-pair' complex because of formation of different species as products of hydrolysis of the complex. Faint purple colour of the solid ferric nitrate or ferric perchlorate aqueous solution in both of which complex formation is negligible has been attributed to absorption by hydrated ferric ion. The yellow colour of the ferric halide or other ferric salt solutions under conditions of pH when formation of collidal ferric hydroxide is prevented has been attributed to the presence of few or all the species like $Fe^{3+}X^{-}$, $Fe^{3+}X_2^{2-}$ $Fe^{3+}X_3^{3-}$, $Fe^{3+}X_4^{4-}$ $Fe^{3+}X_5^{5-}$, $Fe^{3+}X_6^{6-}$, etc., in addition to the species $Fe^{3+}(OH)^{-}$, $Fe^{3+}(OH)_2^{2-}$, etc. (X = Halogen). For the sake of simplicity the number of water molecules (hydration shell) associated with ferric ions have been omitted. The species $Fe^{3+}Cl^{-}$ for example should be represented actually by $Fe^{5+}Cl^{-}(H_2O)_5$, etc.

Farkas and Farkas (1938) explained that the primary light absorption process in aqueous halide ions was associated with electron affinity plus solvation energy of the anion. Rabinowitch (1942) also indicated that the elelctron transfer spectra of cation—anion complexes could be explained in terms of the ionization potential of the cation, electron affinity and solvation energy of the radical formed and solvation energy of the anion. Weiss (1947) suggested that the absorption of aqueous alkali azide in the ultra violet was connected with the electron transfer spectrum, the primary photo chemical process being,

$$N_3^{-} + H_2O \xrightarrow{h\nu} N_3 + (H_2O^{-})$$

Evans and Uri (1949) showed that the atoms and radicals produced by the irradiation of especially ferric ion pair complexes led to polymerization of vinyl compounds in aqueous solution. Evans,

Santappa and Uri (1951) presented a detailed report on the polymerization of vinyl monomers with the ion pairs $Fe^{3+}Cl^-$ and $Fe^{3+}OH^-$ and to some degree with the ion-pair $Fe^{3+}N_3^-$ at 313mμ and 365 mμ. In this paper an exhaustive treatment of behaviour of especially the azide complex is presented.

II. Experimental

The light source from 250-Watt high pressure mercury vapour Lamp (B.T.H.) was rendered parallel by means of a quartz condenser lens and passed through series of filters for isolation of mercury lines 313 mμ, 365 mμ, etc. (*Bowen*, 1946). The light beam after passing through the iris diaphragm entered the window of the thermostat filled with water at $25 \pm 0{\cdot}1°C$ and at the centre of which was mounted the reaction cell whose diameter was 5 cm. and the length in the direction of the optical beam was 4·6 c.m. The lamp output was determined by chemical actinometry using uranyl oxalate solution (Bowen, 1946). Most of the chemicals used were Analar B.D.H. type. Monomers, Methyl methacrylate, acrylonitrile and methacrylic acid were always distilled twice or thrice immediately before use. Before irradiation, the solutions were deaerated by passing through them nitrogen gas which was purified in Fieser's solution. Ferrous ion was determined colorimetrically using o-phenanthroline as the colouring agent. Monomer disappearance was determined either by 'bromine titration' of residual monomer after polymerization or by the weight of the purified and dried polymers. Viscosities and chain lengths of the polymers of methyl methacrylate were determined in A. R. Benzene using Ostwald Viscometer No. 1.

III. Kinetic Results

Under conditions of pH 1 to 4, even ferric perchlorate or nitrate aqueous solutions assume yellow brownish colour which is attributed to the presence of the ion-pair $Fe^{3+}OH^-$ whose concentration is dependent on the pH of the solution. At $pH = O$ (and $[H^+]^* = 3N$) the relative concentration of the hydroxyl ions and consequently the concentration of $Fe^{3+}OH^-$ is minimum. As the pH is increased and provided it does not reach the limit of precipitating collidal ferric hydroxide, the concentration of $Fe^{3+}OH^-$ and the intensity of yellow colour go on increasing. Addi-

* Square brackets indicate molar concentrations.

tion of halide ions or azide ions to the system containing $Fe^{3+}OH^-$ brings about the following equalibria involving the complexes $Fe^{3+}X^-$ etc., or $Fe^{3+}N_3^-$ etc. (X = -halide);

$$Fe^{3+}OH^- + X^- \rightleftharpoons Fe^{3+}X^- + OH^-$$

$$Fe^{3+}X^- + X^- \rightleftharpoons Fe^{3+}X_2^{2-}$$

$$Fe^{3+}X_2^{2-} + X^- \rightleftharpoons Fe^{3+}X_3^{3-}$$

etc.

or $$Fe^{3+}OH^- + N_3^- \rightleftharpoons Fe^{3+}N_3^- + OH^-$$

etc.

The formation of higher halide and azide complexes is facilitated by addition of increasing concentrations of halide or azide ions to the system. By increasing the concentration of ferric ion and keeping the halide ion constant the concentration of the first complex $Fe^+ X^-$ alone is increased. The formation of lower ferric azide complexes is achieved by addition of hydrogen ions ($HClO_4$) which combine with azide ions and form hydrazoic acid whose dissociation constant is depressed by addition of more hydrogen ions. The concentration of lower azide complexes like lower hydroxyl ion complexes is therefore pH dependent. As will be seen from table (1), at pH = O and for a relative concentration of azide ions = 5×10^{-6} M and for concentration of the ferric ion = 2×10^{-4} M, the solution is colourless indicating thereby the absence of any azide complex in solution.

When solutions containing the $Fe^{3+}X^-$ (X = OH or Halide or azide ion) complex and the vinyl monomer are irradiated, the ultimate result is the reduction of ferric to ferrous ion and the oxidation of the anion to a free radical which initiates polymerisation of the vinyl monomer. Concentrations of ferric ion over a range of 10^{-1} to 10^{-5} M were found to be effective (Evans et. al, 1951) for the formation of active ion-pair sensitizers. For a study of kinetics of polymerization, knowledge of concentration and light absorption fraction of the sensitizer are important.

Determination of concentration and total light absorption fractions ($k\varepsilon$) *of the ion-pairs*:—(a) *To calculate* $k\varepsilon$ ($Fe^{3+}OH^-$)*

* K_ε ($Fe^{3+}OH^-$) reprersents light absorption fraction K_ε by $Fe^{3+}OH^-$.

TABLE I

Ion pair		Relative concentrations in molarity and colour						
$Fe^{3+}OH^-$	$[Fe^{3+}]$	0·1	0·1	0·1	0·1	0·1	0·1	0·1
	$[OH^-]$	1	0·6	0·3	0·1	0·02	0·01	0·005
	$[H^+)$	10^{-2}	2×10^{-2}	5×10^{-2}	10^{-1}	5×10^{-1}	1	3
	Colour	Yellow	Yellow	Yellow	very faint yellow	colourless	colourless	colourless
$Fe^{3+}Cl^-$ and higher complexes	$[Fe^{3+}]$	0·1	0·1	0·1	0·1	0·1	0·1	0·1
	$[Cl^-]$	0·01	0·02	0·05	0·1	0·5	1·0	3·0
	Colour	Yellow	⟶	⟶	Bright green yellow	⟶	⟶	Brownish yellow
$Fe^{3+}N_3^-$	$[Fe^{3+}]$	2×10^{-4}	2×10^{-4}	2×10^{-1}	2×10^{-4}	2×10^{-4}	2×10^{-4}	
	$[H^+]$	2×10^{-2}	5×10^{-2}	10^{-1}	2×10^{-1}	5×10^{-1}	1	
	$[Na\,N_3]$	2×10^{-2}	2×10^{-2}	2×10^{-2}	2×10^{-2}	2×10^{-2}	2×10^{-2}	
	$[N^-_3]$	2×10^{-4}	10^{-4}	5×10^{-5}	2×10^{-5}	10^{-5}	5×10^{-6}	
	Colour	Red....	⟶		Pale Red	⟶ ...	colourless	

the following data for example are considered: $[Fe(Clo_4)_3] = 10^{-2}M$; $pH = 1$; wavelength, $(\lambda) = 313$ mμ; ionic strength $(\mu) = 0{\cdot}2$. From Rabinowitch and Stockmayer's (1942) relation between the log of association constant for $Fe^{3+}OH^-$, (K_H) and the ionic strength of the solution (μ) we get,

$$\log K_H = \log \frac{[Fe^{3+}OH^-]}{[Fe^{3+}]} + \log H^+$$

$$\therefore \log \left[\frac{Fe^{3+}OH^-}{Fe^{3+}} \right] = 1{\cdot}5 \text{ or } \left[\frac{Fe^{3+}OH^-}{Fe^{3+}} \right] = 32$$

From the ratio of $[Fe^{3+}OH^-/Fe^{3+}]$ and also $[Fe^{3+}OH^-]+[Fe^{3+}]= 10^{-2}M$, the actual concentrations of Fe^{3+} as well as $Fe^{3+}OH^-$ can be calculated: $[Fe^{3+}] = C_1 = 9{\cdot}7 \times 10^{-3}$; $[Fe^{3+}OH^-] = C_2 = 0{\cdot}3 \times 10^{-3}$. If ε_1 and ε_2 are the molar extinction coefficients of Fe^{3+} and $Fe^{3+}OH^-$ respectively and α_1 and α_2, their respective light absorption fractions and since $\varepsilon_1 = 25{\cdot}12$, $\varepsilon_2 = 2512$ (Rabinowitch and Stockmayer, 1942) and $\alpha_1 = C_1\varepsilon_1 / (C_1\varepsilon_1 + C_2\varepsilon_2)$ etc. the values arrived at will be $\alpha_1 = 0{\cdot}2443$ and $\alpha_2 = 0{\cdot}7557$.

If I_o = incident light and I = transmitted light, the fraction of light absorbed by Fe^{3+} plus $Fe^{3+}OH^-$ will be equal to $I_o - I/I_o$ which can be calculated from the well-known relation $\log I_o/I = (\varepsilon_1 C_1 + \varepsilon_2 C_2)\, d$, where d = length of the irradiated solution which is 4·6 c.m. in our case. $\log I_o/I$ may be obtained by either (a) direct reading on the spectro photo-meter or (b) calculation from the known values of ε_1, C_1, ε_2, C_2, d, etc. If the absorption is incomplete $(I_o - I)/I$ will be equal to unity; if absorption is incomplete, it will be less than unity. Then k_ε for ferric ion will be given by $(I_o - I)/I \times \alpha_1$ and for $Fe^{3+}OH^-$ it is $(I_o - I)/I \times \alpha_2$. Since the absorption in the present example is found to be omplete, k_ε (Fe^{3+}) will be equal to 0·2443 and k_ε $(Fe^{3+}OH^-)$ will be 0·7557.

(b) k_ε $(Fe^{3+}Cl^-)$ may be calculated from the following data; $[Fe(Clo_4)_3] = 10^{-3}M$; $[HCl] = 0{\cdot}5N$; $\lambda = 313$ mμ; $\mu = 0{\cdot}2$; considering the following equalibria

$$Fe^{3+} + H_2O \rightleftharpoons Fe^{3+}OH^- + H^+ \ldots\ldots K_H^*$$

$$Fe^{3+}OH^- + Cl^- \rightleftharpoons Fe^{3+}Cl^- + OH^-$$

$$Fe^{3+} + Cl^- \rightleftharpoons Fe^{3+}Cl^- \ldots\ldots K = 30$$

* Ks refer to association constants.

And remembering that after the equalibria is established the following relations hold,

$$[Fe^{3+}] + [Fe^{3+}OH^-] + [Fe^{3+}Cl^-] = 10^{-3}M$$
$$\text{and } [Fe^{3+}Cl^-] + [Cl^-] \ldots = 5 \times 10^{-2}M$$

K_H may be calculated which in this case is found to be equal to $3{\cdot}3 \times 10^{-3}$ and

$$\therefore [Fe^{3+}OH^-] = 6{\cdot}6 \times 10^{-2}\,[Fe^{3+}].$$

Also since $[Cl^-] + 30\,[Fe^{3+}]\,[Cl^-] = 5 \times 10^{-2}$

$$\therefore [Fe^{3+}Cl^-] = \frac{30[Fe^{3+}] + 0{\cdot}05}{1 + 30\,[Fe^{3+}]}$$

It is now easy to calculate the molar concentrations of various species: $[Fe^{3+}] = 3{\cdot}9 \times 10^{-4}$; $[Cl^-] = 4{\cdot}9 \times 10^{-2}$; $[Fe^{3+}Cl^-] = 59 \times 10^{-4}$ and $[Fe^{3+}OH^-] = 1{\cdot}9 \times 10^{-5}$. Now if ε_3, C_3 and α_3 are the molar extinction coefficient at 313 mμ (3800), concentration and light absorption fraction respectively for the ion pair $Fe^{3+}Cl^-$ then, $\alpha_3 = C_3\varepsilon_3/C_1\varepsilon_1 + C_2\varepsilon_2 + C_3\varepsilon_3)$. The value α_3 has been found to be 0·96. Absorption having been found to be complete, k_ε $(Fe^{3+}Cl^-)$ will be 0·96.

(c) k_ε $(Fe^{3+}N_3^-)$: $[Fe(Clo_4)_3] = 10^{-2}M$;

$[NaN_3] = 2 \times 10^{-2}M$; $[HClo_4] = 0{\cdot}3N$;

The following equalibria should be considered:

$$Fe^{3+} + H_2O \rightleftharpoons Fe^{3+}OH^- + H^+ \ldots\ldots K_H$$

$$N_3^- + H^+ \rightleftharpoons N_3H \ldots\ldots\ldots K_{N_3H} = 5{\cdot}56 \times 10^4$$

$$Fe^{3+}OH^- + N_3^- \rightleftharpoons Fe^{3+}N_3^- + OH^-$$

$$Fe^{3+} + N_3^- \rightleftharpoons Fe^{3+}N_3^- \ldots\ldots K_{FeN_3} = 1{\cdot}3 \times 10^4$$

After the equalibria have been established the following relations hold good

$$[Fe^{3+}] + [Fe^{3+}OH^-] + [Fe^{3+}N_3^-] = 10^{-2}M$$

$$\text{and } [N_3H] + [N_3^-] + [Fe^{3+}N_3^-] = 2 \times 10^{-2}M.$$

By calculations similar to those for k_ε $(Fe^{3+}Cl^-)$ and remembering that the extinction coefficient (ε) for ferric azide at 313 mμ = 5000 (Uri, unpublished results) the values of k_ε $(Fe^{3+}N_3^-)$ may be

calculated. These values which are pH dependent are given in table 2.

TABLE 2

pH	μ	K_H	$[Fe^{3+}N_3^-] \times 10^4$	$[Fe^{3+}OH^-] \times 10^4$	$[Fe^{3+}] \times 10^4$	k $(Fe^{3+}N_3^-)$
0	1·07	7·5	0·46	0·76	98·54	0·2
0·6	0·345	3·28	1·8	1·258	96:16	0·77
1·0	0·17	3·09	4·04	2·815	91·07	0·915
1·3	0·12	3·162	7·16	5·307	83·97	0·935

Linear variations of k_e s for $Fe^{3+}N_3^-$ and $Fe^{3+}OH^-$ with pH and k_e for $Fe^{3+}Cl^-$ with the concentration of the ferric ion have been observed (Fig. 1).

(i) k_e.—Since concentration of the ferric azide is pH dependent, it is seen from table 3 that dFe^{2+}/dt also increases with increasing k_e as well as pH (Fig. 1) for $[Fe(Clo_4)_3] = 10^{-2}M$; $[NaN_3] = 2 \times 10^{-2}M$ [Acrylonitrile] = 1·0 M and Intensity of light = $6·9 \times 10^{-5}$ N$h\nu$ units/hr.

TABLE 3

pH	k_e	dFe^{2+}/dt (moles/hr.) $\times 10^6$
0	0·2	3·9
0·6	0·77	18·3
1·0	0·915	23·0
1·3	0·935	24·8

The linearity between k_ε on the one hand and the monomer disappearance as well as chain length on the other hand which have been well established with ferric chloride complex and methyl-methacrylate monomer (Evans, et al, 1951) could not be established for the ferric azide complex and any of the monomers. Rate of monomer disappearance could not be accurately determined with the azide initiator because of large difference in the value of dM/dt between 'bromine titration' method and weight of the polymer. The solution containing $[Fe(Clo_4)_3] = 10^{-2}M$; $[H^+] = 0{\cdot}5N$; $[NaN_3] = 2 \times 10^{-2}M$; [Methyl-methacrylate] $= 0{\cdot}1$ M was thoroughly deaerated and irradiated with 313 mμ for over twelve hours and the results given in table 4 have been obtained.

TABLE 4

Number of moles of methyl metha-crylate irradiated	$= 6{\cdot}3 \times 10^{-3}$ moles
dM/dt by weight of the polymer	$= 9 \times 10^{-6}$ moles
dM/dt by bromine titration of residual monomer.	$= 3{\cdot}6 \times 10^{-3}$ moles

The chain length of the azide initiated polymer could not be determined accurately because of the high molecular weight of the polymer and low nitrogen content. Determination of nitrogen in the polymer colorimetrically using Nessler's reagent gave high results of nitrogen. Azide initiated polymer of methyl-methacrylate prepared after irradiating the system $[Fe(Clo_4)_3] = 10^{-2}M$; $[HClo_4] = 10^{-3}M$; $[NaN_3] = 2 \times 10^{-2}M$ and [Methyl methacrylate] $= 0{\cdot}1$ M for about 8 hours was purified and dried by the usual technique. Molecular weight of the polymer was determined by the Baxendale, Evans and Bywater's (1946) viscosity method and then nitrogen content of the polymer was determined colorimetrically. For the sake of comparison the hydrazine initiated polymer of methyl methacrylate which was prepared after irradiating the system consisting of 4 ml of 50% hydrazine and 1% of methyl methacrylate for about 8 hours was also purified and dried and the corresponding molecular weight and nitrogen content of the polymer were also determined (Table 5).

TABLE 5

Molecular weight of azide initiated methyl methacrylate polymer	.. 85000 to 100000
Molecular weight of hydrazine initiated polymer	..35000 to 55000
Nitrogen content for azide initiated polymer	16 atoms of nitrogen ..per 1 mole of polymer
Nitrogen content for hydrazine initiated polymer	12 atoms of nitrogen ..per mole of polymer.

The maximum quantity of nitrogen in the polymer used should be of the order of 10^{-6} Molar assuming only six atoms of nitrogen per mole of polymer. It is obvious from the "Spekkar" readings of log I_o/I for NH_3 given in table 6 that the readings are unreliable for measurement of ammonia concentrations of as low as 5×10^{-5} M with 4 c.m. cell.

TABLE 6

$[NH_3]$	log I_o/I	
	4 c.m. cell	1 c.m. cell
6×10^{-4}	1·3	0·479
4×10^{-4}	1·06	0·375
10^{-4}	0·43	Not
8×10^{-5}	0·25	measurable
5×10^{-5}	0·16	„
2×10^{-5}	Not measurable	„
10^{-5}	„	„
8×10^{-6}	„	„

(ii) Light intensity I: Variation of light intensity was achieved by using an Iris diaphragm in front of the lamp. The linearity relation between dFe^{2+}/dt and the light intensity in case of $Fe^{3+}OH^-$ as well as $Fe^{3+}Cl^-$ sensitizers has been found (Evans, et al, 1951) to hold up to an intensity of 8×10^{-5} N$h\nu$ units per hour and for higher intensities a departure from the linearity was

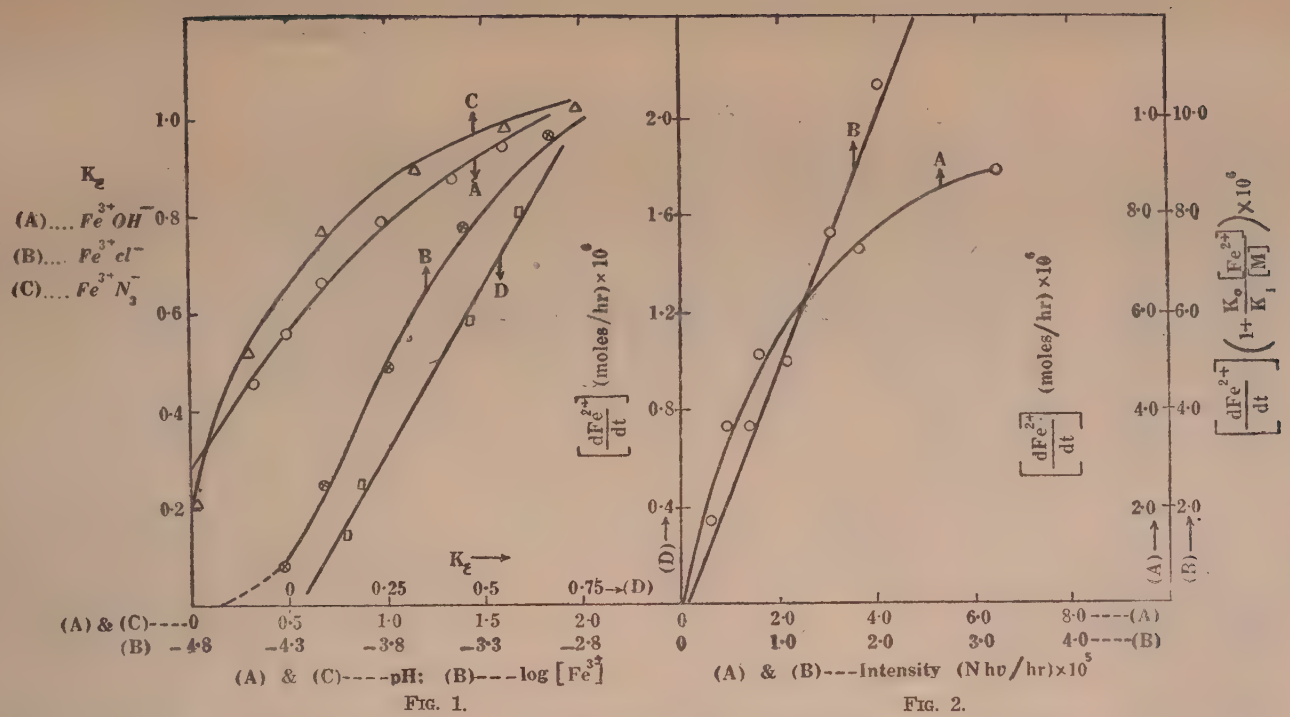

FIG. 1. FIG. 2.

FIG. 1. Curves A & C show the variation of k_ε with pH for $Fe^{3+}OH^-$ and $Fe^{3+}N_3^-$ respectively and curve B shows variation of k_ε with $[Fe^{3+}]$ for $Fe^{3+}Cl^-$. Curve D shows the linear variation of k_ε with dFe^{2+}/dt for $Fe^{3+}N_3^-$ in the system $[Fe(Clo_4)_3]=10^{-2}$M; $[NaN_3]=2\times10^{-2}$M and $I=6\cdot9\times10^{-5}$ $Nh\nu$ units per hour.

FIG. 2. Curve A shows the dependence of dFe^{2+}/dt and curve B shows the dependence of $dFe^{2+}/dt(1+k_0[Fe^{2+}]/k_1[M])$ on the intensity of light with $Fe^{3+}N_3^-$ initiator; $[Fe(Clo_4)_3]=0\cdot01$ M; $[NaN_3]=2\times10^{-2}$M; pH=2·0 [Acryloritrile]=1·0M.

observed. For $Fe^{3+}N_3^-$ initiator, the departure from linearity started at intensities as low as 2-3 $\times 10^{-5}$ N ν units per hour. On the other hand when $(d\ Fe^{2+}/dt)\{I + (k_o\ Fe^{2+}/k_i[M])\}$ which took into account the disappearance of ferrous ion by the secondary dark back reaction, was plotted against light intensity a uniform variation (Santappa, 1951) was observed (Table 7; Fig. 2).

TABLE 7

$[Fe(Clo_4)_3] = 0{\cdot}01$ M; $[NaN_3] = 2 \times 10^{-2}$ M; pH = 2; [Acrylonitrite]=1·0 M; $k_o/k_i = 5 \times 10^2$ (Evaluation of k_o/k_i is indicated elsewhere in this paper).

Intensity ($N h\nu$/hr) $\times 10^5$	$d\,Fe^{2+}/dt$ (moles/hr) $\times 10^6$	Mean $[Fe^{2+}]$ (moles) $\times 10^5$	$(dFe^{2+}/dt)\left(\frac{I+k_oFe^{2+}}{k_i[M]}\right)$ $\times 10^6$
6·94	7·98	5·7	8·25
5·30	7·10	5·07	7·32
3·89	6·3	4·5	6·47
1·97	4·83	3·45	4·93
0·93	3·3	2·36	3·35
0·8	2·37	1·7	2·4
0·28	1·8	1·29	1·82

dM/dt and square root light intensity function as well as chain length of polymer versus reciprocal square root light intensity function both of which were established for $Fe^{3+}OH^-$ as well as $Fe^{3+}Cl^-$, (Evans et. al, 1951) could not be unequivocally established for $Fe^{3+}N_3^-$ because of difficulty of determining dM/dt and chain length of the polymers.

(iii) Monomer Concentration :

A study of the relation between monomer concentration and rate of ferrous ion production in case of $Fe^{3+}OH^-$ as well as $Fe^{3+}Cl^-$ initiators showed (Evans et. al, 1951) that a constant quantum yield with regard to ferrous ion was obtained in each case. This anamalous behaviour which must be attributed to impurities will be explained elsewhere in greater detail. On the other hand, in the case of $Fe^{3+}N_3^-$ as the initiator the results of

variation of rate of ferrous ion production with change of monomer concentration followed the linearity (Santappa, 1951) relation well (Fig. 3; Table 8). γ_{net} represents quantum yield for ferrous ion production.

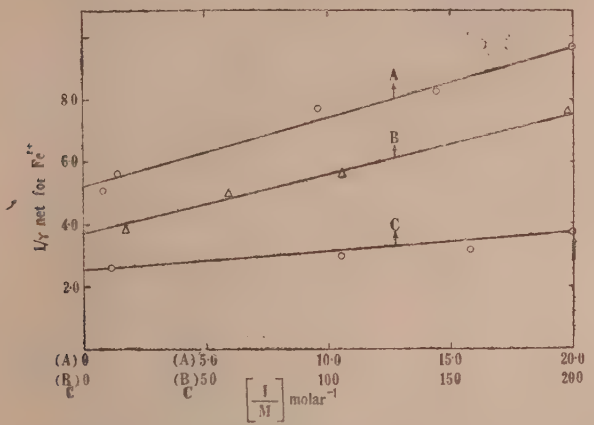

FIG. 3. Shows variation of $1/\gamma_{net}$ with reciprocal monomer concentration with $Fe^{3+}N_3^-$ at pH=0·5 to 0·6 for acrylonitrile (Curve A), methyl methacrylate (Curve B) and methacrylic acid (Curve C).

TABLE 8

$[Fe^{3+}] = 10^{-2}$ M; $[NaN_3] = 2 \times 10^{-2}$ M; $\lambda = 313$ mμ; $I = 6{\cdot}9 \times 10^{-5}$ Nhυ/hr.

Monomer	[M]	pH	dFe^{2+}/dt (moles/hr) $\times 10^6$	γ_{net}
Acrylonitrite ..	0·01	1-1·1	6·3	0·1
	0·05	„	10·3	0·16
	0·1	„	14·8	0·24
	0·5	„	18·8	0·30
Methyl methacrylate ..	10^{-4}	„	6·16	0·1
	10^{-3}	„	10·3	0·16
	10^{-2}	„	18·8	0·3
	0·1	„	35·0	0·55

The linear relation between monomer concentration on the one hand and the rate of monomer disappearance as well as chain length on the other hand established for acrylonitrite as well as methylmethacrylate and $Fe^{3+}Cl^-$ ion-pair sensitizer (Evans, et. al, 1951) could not be established with $Fe^{+}N^{-}_{3}$ for the obvious reasons.

(iv) Effect of initially added ferrous ion and ferrous ion formed during the reaction is the same. In either case due to secondary back reaction, $d[Fe^{2+}]/dt$ must decrease with time or with increase of the mean ferrous ion concentration which is defined as the sum of ferrous ion initially present plus one half ferrous ion produced during the time interval. In the range of mean ferrous ion of concentration $2{\cdot}5 \times 10^{-5}$M to $12{\cdot}5 \times 10^{-5}$M a linear plot for mean ferrous ion with $I/(d[Fe^{2+}]/dt)$ in case of $Fe^{3+}OH^-$ as well as $Fe^{3+}Cl^-$ were obtained. But in case of azide initiator even with nil initially added ferrous ion, ferrous ion produced during reaction was of the order of 5×10^{-4}M. When initially added ferrous ion was of the order of $2{\cdot}5 \times 10^{-4}$M; total ferrous ion produced dropped to 4×10^{-4}M, thus bringing up the initial mean ferrous from $2{\cdot}5 \times 10^{-4}$ to $3{\cdot}25 \times 10^{-4}$M. With higher concentrations of initially added ferrous the experimental error in the evaluation of $d[Fe^{2+}]/dt$ and mean ferrous became quite considerable.

(v) *Quantum yield.* (γ) The quantum yield with regard to ferrous ion production was found to depend upon (a) the initiator species (therefore upon pH in case of $Fe^{3+}OH^-$ and $Fe^{3+}N^{-}_{3}$ and upon $[Fe^{3+}]$ in case of $Fe^{3+}Cl^-$) as well as (b) the wavelength used. For $Fe^{3+}OH^-$ and $Fe^{3+}Cl^-$, it was found that γ was independent of type and concentration of the monomer used. In case of azide complex quantum yields were also found to be different for different monomers and their various concentrations. γ with $Fe^{3+}OH^-$ and $Fe^{3+}Cl^-$ was more or less equal at 313 and 365 mμ, but dropped steeply when the limit of the visible was reached. But in case of $Fe^{3+}N_3^-$ which has two absorption peaks, one at $\sim$ 300 mμ and another at $\sim$ 470 mμ it was found that γ reached a maximum of $\sim$ 0·5 in the U.V. and a tendency to rise for the second maximum also at $\sim$ 435 mμ was observed. This latter rise is to be attributed to absorption in the visible rather than to tail end of the $\sim$ 300 mμ band. Maximum values of quantum yields obtained were: With $Fe^{3+}OH^-$ $\sim$ 0·05; $Fe^{3+}Cl$ $\sim$ 0·13 and $Fe^{3+}N_3$ $\sim$ 0·5.

Table (9) gives values of quantum yields with $Fe^{3+}N^{-}_{3}$ with various monomers at their maximum concentrations and at different

pH for 313 mμ line as well as with acrylonitrite at different wave lengths.

TABLE 9

Monomer	pH	γ	λ
Acrylonitrite	1·0 — 1·1	0·4	(313 mμ)
		0·209	(365 „)
		0·103	(405 „)
		0·120	(435 „)
„	0·5 — 1·1	0·5	(313 „)
Methyl methacrylate	1·0 — 1·1	0·5	(313 „)
„	0·5 — 0·6	0·27	(313 „)
Methacrylic acid	1 — 1·1	0·5	(313 „)
„	0·5 — 0·6	0·5	(313 „)

Quantum yield with regard to monomer disappearance was found to be dependent on (a) the type of monomer, (b) concentration of the monomer, (c) the light intensity and (d) the initiator species used. In case of $Fe^{3+}N_3^-$ it has been already indicated in this paper that dM/dt by 'bromine titration' and weight of the dried polymers do not tally and hence correct value for the quantum yield with regard to dM/dt must await further work.

IV. *Theoretical Considerations and Discussion*

The following reaction scheme includes those reactions which are likely to occur. The rate constants (ks) for each reaction are differentiated by their suffixes.

(1) Light absorption :

$$Fe^{3+}N_3^- \xrightarrow[h\nu]{k\varepsilon\, I} Fe^{2+}N_3 \qquad k_\varepsilon = \text{Light absorption fraction.}$$

$h\nu$ have the usual significance, I = Intensity of light,

(2) Primary dark back reaction :

$$Fe^{2+}N_3 \xrightarrow{k_d} Fe^{3+}N_3^-$$

(3) Initiation of polymerization by the primary product $Fe^{2+}N_3$,

$$Fe^{2+}N_3 + M \xrightarrow{k_i} Fe^{2+} + N_3{-}M^-$$

where M = Vinyl monomer.

(4) Separation of the primary product :

$$Fe^{2+}N_3 \xrightarrow{k_s} Fe^{2+} + N_3$$

(5) Secondary dark back reaction :

$$Fe^{2+} + N_3 \xrightarrow{k_o} Fe^{3+} + N_3^-$$

(6) Initiation of polymerization by free radicals N_3,

$$N_3 + M \xrightarrow{k_i} N_3 - M -$$

(7) Propagation of polymerization :

$$N_3{-}M- + M \xrightarrow{k_p} N_3{-}M{-}M-$$

$$N_3{-}M{-}M- + M \xrightarrow{k_p} N_3{-}M{-}M{-}M-$$

$$N_3{-}(M)_n^- + M \xrightarrow{k} N_3{-}(M)_{n+1}^-$$

(8) Termination of polymerization by (i) disproportionation by :

(a) free radical $Fe^{2+}N_3$

$$N_3{-}(M)_{n+1}^- + Fe^{2+}N_3 \xrightarrow{k_{t1}} N_3{-}(M)_{n+1} N_3 + Fe^{2+}$$

And or by (b) free radical N_3

$$N_3-(M)_{n+1}- + N_3 \xrightarrow{k_{t2}} N_3-(M)_{n+1}-N_3$$

And or by (ii) Recombination of active endings :

$$N_3-(M)_{n+1}- + -(M)_{n+1}-N_3 \xrightarrow{k_t} N_3-(M)_{n+1}-(M)_{n+1}-N_3$$

By making use of the above reaction scheme expressions for the rate of ferrous ion production dFe^{2+}/dt and rate of monomer disappearance dM/dt might be obtained. Assumptions regarding occurence or non-occurence of certain steps in the above scheme lead to alternative expressions for dFe^{2+}/dt and dM/dt and eventually correlation of the experimental data with various expressions will suggest the correct reaction scheme. For example the following possibilities might be considered.

Possibility 1 : Initiation of polymerisation by the primary product $Fe^{2+}N_3$ alone. Steps (4), (5) and (6) in the above scheme should therefore be neglected. Under possibility I, two types of termination reactions (a) Disproportionation by free radicals, $Fe^{2+}N_3$ or (b) Recombination of active endings, should be considered. Disproportionation and recombination will be represented by I (a) and I (b) respectively.

Possibility 2 : Initiation of polymerization by free radicals N_3 only. Again terminations by disproportionation or recombination are represented by 2 (a) and 2 (b) respectively.

Possibility 3 : Initiation by the free radicals $Fe^{2+}N_3$ as well as N_3. The two types of terminations 3 (a) and 3 (b) must be considered.

Consider I (a). The following assumptions (i) and (ii) found valid in all polymerization kinetics need to be applied for all the derivations: (i) The rate constants for propagation and termination reactions remain constant throughout the course of polymerization and are therefore independent of chain length and (ii) assuming stationary state concentrations for the free radical species, $Fe^{2+}N_3$; N_3 and $N_3-(M)_n-$ it follows that $d[Fe^{2+}N_3]/dt = 0$; $d[N_3]/dt = 0$; $d[N_3-(M)-]/dt = 0$

We then obtain

$$\frac{d[Fe^{2+}N_3]}{dt} = k_\varepsilon \; I - k_d[Fe^{2+}N_3] - k_i[Fe^{2+}N_3][M] = 0$$

$$\therefore [Fe^{2+}N_3] = k_\varepsilon I/(k_d + k_i[M])$$

The rate of ferrous ion production is then given by

$$dFe^{2+}/dt = k_i[Fe^{2+}N_3][M] = k_i k_\varepsilon I[M]/(k_d + k_i[M])$$

If it is assumed that $k_i[M] > k_d$

then $dFe^{2+}/dt = k\varepsilon I$

and the net quantum yield with regard to ferrous ion will be,

$$\gamma_{net} = I.$$

If the monomer concentration is so small that $k_d \gg k_i[M]$ then

$$dFe^{2+}/dt = k_\varepsilon I k_i[M]/k_d$$

and $$\gamma_{net} = k_i[M]/k_d$$

Assuming stationary state method and termination by disproportionation by the free radical $Fe^{2+}N_3$ only, the concentration of the growing polymer chain will be given by:

$$d[N_3-(M)_n-]/dt = k_i[Fe^{2+}N_3][M] - k_{t1}[Fe^{2+}N_3][N_3-(M)_n-] = 0$$

$$\therefore [N_3-(M)_n-] = k_i[M]/k_{t1}$$

The rate of monomer disappearance is given by monomer consumed for propagation and initiation. Assuming that monomer consumed for initiation reaction is very small, we get:

$$dM/dt = k_p[N_3-(M)_n-][M] = k_p k_i[M]^2/k_{t1}$$

Consider I (b): This leads to the same expression for $d\,Fe^{2+}/dt$ but a different expression for dM/dt.

$$d[N_3-(M)_n-]/dt = k_i[M][Fe^{2+}N_3] - k_t[N_3-(M)_n-]^2 = 0$$

$$\therefore [N_3-(M)_n-] = \{k_i[M][Fe^{2+}N_3]/k_t\}^{1/2}$$

$$dM/dt = k_p[N_3-(M)_n-][M] = k_p[M]^{3/2}\{k_i k_\varepsilon I/k_t (k_d + k_i[M])\}^{1/2}$$

If $k_i[M] \gg k_d$ then $dM/dt = k_p[M]\{k_\varepsilon I/k_t\}^{\frac{1}{2}}$

For very small monomer concentrations so that $k_i[M]$ becomes small compared with k_d we obtain

$$dM/dt = k_p[M]^{3/2}\{(k_i k_\varepsilon I)/k_t k_d\}^{\frac{1}{2}}$$

Consider 2 (*a*).

$$d[Fe^{2+}N_3]/dt = k_\varepsilon I - k_d[Fe^{2+}][N_3] - k_s[Fe^{2+}N_3] = 0$$

$$\therefore [Fe^{2+}N_3] = k_\varepsilon I/(k_d + k_s)$$

$$d[N_3]/dt = k_s[Fe^{2+}N_3] - k_o[Fe^{2+}][N_3] - k_i[N_3][M] = 0$$

$$\therefore [N_3] = k_s[Fe^{2+}N_3]/k_i[M] + k_o[Fe^{2+}]$$

$$= k_s k_\varepsilon I/(k_i[M] + k_o[Fe^{2+}])(k_d + k_s)$$

$$dFe^{2+}/dt = k_s[Fe^{2+}N_3] - k_o[Fe^{2+}][N_3]$$

$$= k_s k_\varepsilon I/(k_d + k_s) - (k_o[Fe^{2+}]k_s k_\varepsilon I)/$$

$$(k_i[M] + k_o[Fe^{2+}])(k_d + k_s)$$

$$= k_s k_\varepsilon I/(k_d + k_s)\{k_i[M]/(k_i[M] + k_o[Fe^{2+}])\}$$

$$\gamma_{net} = k_s/(k_d + k_s)\{k_i[M]/(k_i[M] + k_o[Fe^{2+}])\}$$

Also dFe^{2+}/dt (maximum) $= k_s k_\varepsilon I/(k_d + k_s)$; γ (max.) $= k_s/(k_d + k_s)$ if it is assumed $k_i[M] > k_o[Fe^{2+}]$

For termination by disproportionation by radicals N_3 only the concentration of the growing chain is given by,

$$d[N_3 - (M)_n -]/dt = k_i[N_3][M] - k_{t2}[N_3][N_3 - (M)_n -] = 0$$

$$\therefore [N_3 - (M)_n -] = k_i[M]/k_{t2}.$$

$$\therefore dM/dt = k_p[N_3 - (M)_n -][M] = k_p k_i[M]^2/k_{t2}$$

Consider 2 (*b*). The expression for dFe^{2+}/dt for 2 (b) will be same as for 2 (*a*); but the expression for dM/dt will be a different one. Assuming termination by recombination, the concentration of the growing radical will be given by

$$d[N_3 - (M)_n -] \mid dt = k_i[M][N_3] - k_t[N_3 - (M)_n -]^2 = 0$$

$$\therefore \quad [N_3 - (M)_n -] = \{k_i[M][N_3] \mid k_t\}^{1/2}$$

$$\therefore \quad dM \mid d_t = k_p[N_3 - (M)_n -][M]$$

$$= k_p[M]\,(k_i[M] \mid k_t)^{1/2}$$

$$\{k_s k_\varepsilon\, I \mid (k_i[M] + k_o[Fe^{2+}])\,(k_d + k_s)\}^{1/2}$$

If $k_i[M] \gg k_o[Fe^{2+}]$ then

$$dM \mid dt = k_p[M]\{k_s k_\varepsilon\, I \mid k_t(k_s + k_d)\}^{1/2}$$

Consider 3 (*a*).

$$d[Fe^{2+}N_3] \mid dt = k_\varepsilon\, I - k_d[Fe^{2+}N_3] - k_i'[Fe^{2+}N_3][M] - k_s[Fe^{2+}N_3] = 0$$

$$\therefore \quad [Fe^{2+}N_3] = k_\varepsilon\, I \mid (k_d + k_s + k_i'[M])$$

$$d[N_3] \mid dt = k_s[Fe^{2+}N_3] - k_o[Fe^{2+}][N_3] - k_i[N_3][M] = 0$$

$$\therefore \quad [N_3] = k_s[Fe^{2+}N_3] \mid (k_i[M] + k_o[Fe^{2+}])$$

$$= k_s k_\varepsilon\, I \mid (k_i[M] + k_o[Fe^{2+}])\,(k_d + k_s + k_i'[M])$$

$$dFe^{2+} \mid dt = k_i'[Fe^{2+}N_3][M] + k_s[Fe^{2+}N_3] - k_o[Fe^{2+}][N_3]$$

$$= \frac{k_s k_\varepsilon'\, I}{(k_d + k_s + k_i'[M])} \left\{ \frac{k_i'[M]}{k_s} + \frac{k_i[M]}{k_o[Fe^{2+}] + k_i[M]} \right\}$$

Considering termination by disproportionation by radicals $Fe^{2+}N_3$ as well as N_3, the concentration of the radical chains is given by :

$$d[N_3 - (M)_n -] \mid dt = k_i'[M]\,[Fe^{2+}N_3] + k_i[N_3][M] - k_{t1}[N_3 - (M)_n -][Fe^{2+}N_3] - k_{t2}[N_3 - (M)_n -][N_3] = 0$$

$$\therefore \frac{[N_3 - (M)_n -]}{dt} = \frac{k_i[M][Fe^{2+}N_3] + k_i[M][N_3]}{k_{t1}[Fe^{2+}N_3] + k_{t2}[N_3]}$$

Rate of monomer disappearance is given by

$$\frac{dM}{dt} = k_p[N_3 - (M)_n -][M]$$

$$= k_p[M]^2 \left\{ \frac{k_i'[Fe^{2+}N_3] + k_i[N_3]}{k_{t1}[Fe^{2+}N_3] + k_{t2}[N_3]} \right\}$$

$$= k_p[M]^2 \left\{ \frac{k_i'(k_i[M] + k_o[Fe^{2+}]) + k_i}{k_{t1}(k_i[M] + k_o[Fe^{2+}]) + k_{t2}} \right\}$$

From this expression, dM/dt for 1 (a) as well as 2 (a), can also be derived by making suitable assumptions.

Consider 3 (*b*). Expression for dFe^{2+}/dt will be same as in 3 (a). Assuming termination by recombination, the concentration of the growing radicals is given by,

$$d[N_3-(M)_n-] \mid dt = k_i'[M][Fe^{2+}N_3] + k_i[M][N_3] - [N_3-(M)_n-]^2 k_t = 0$$

$$\therefore [N_3-(M)_n-] = \{ (k_i'[M][Fe^{2+}N_3] + k_i[M][N_3]) \mid k_t \}^{1/2}$$

$$dM \mid dt = k_p[N_3-(M)_n-][M]$$

$$= k_p[M] \{ k_s k_e I \mid k_t (k_d + k_s + k_i'[M]) \}^{1/2}$$

$$= k_p[M] [(k_s k_e I \mid k_t (k_d + k_s + k_o[Fe^{2+}]) (k_i'M \mid k_s) + (k_iM \mid k_i[M] + k_o[Fe^{2+}])]^{1/2}$$

Chain lengths: For termination by disproportionation the chain length is given by the ratio, rate of monomer disappearance : birth rate of the chains or the ratio $dM/dt : dFe^{2+}/dt$. For termination by combination the chain length is given by the ratio, $2\,dM/dt$: birth rate of the chains or $dM \mid dt : \frac{dFe^{2+}}{dt} \mid 2$. The following expressions for chain lengths (n) may then be obtained for every possibility 1 (a), 1 (b), 2 (a), etc.

$$n_{1a} = k_p[M](k_d + k_i'[M]) \mid k_{t1} k_e I$$

$$n_{1b} = 2k_p[M](k_d + k_i'[M]) \mid (k_t k_d k_e I)^{1/2}$$

$$n_{2a} = k_p[M](k_i[M] + k_o[Fe^{2+}])(k_d + k_s) \mid (k_{t2} k_s k_e I)$$

$$n_{2b} = 2k_p[M](k_i[M] + k_o[Fe^{2+}]) \mid k_i[M] \left[\frac{k_t k_s k_e I}{k_s + k_d} \right]^{1/2}$$

etc., etc.

Similar expressions might be obtained for possibilities 3 (a) and 3 (b). Simplifications of these expressions might be obtained by

making certain justifiable assumptions; that (i) $k\varepsilon$ is nearly unity, (ii) $k_i[M] \gg k_d$ for high monomer concentrations; (iii) $k_d \gg k_i[M]$ for high monomer concentrations. Based on these assumptions the expression for chain length under the possibility 2 (b) for example for very low monomer concentrations, (iv) $k_i[M] \gg k_o[Fe^{2+}]$ will be reduced to

$$n_{2b} = 2k_p[M] \mid [k_i k_s k_e I/(k_d + k_s)]^{1/2}$$

Energy and Electron transfer : The energy ($\triangle$ E) corresponding to the light absorption and electron transfer in

$Fe^{3+}N_3^- \xrightarrow{h\nu} Fe^{2+}N_3$ is given by

$$\triangle E = \triangle H + I_{Fe^{2+}} - E_{N_3} - S_{N_3^-} + S_{N_3} + Q$$

where $\triangle H$ = Energy difference between the complex $Fe^{3+}N_3^-$ and the fully dissociated and hydrated state $Fe^{3+}(aq) + N_3^-(aq)$ $= -4{\cdot}3$ K cal.

$I_{Fe^{2+}}$ = Ionization potential of ferrous ion in aqueous solution $= 97$ Kcal

E_{N_3} = Electron affinity of azide radical in aqueous solution.

$S_{N_3^-}$ = Solvation energy of the azide ion

$(S_{N_3^-} + E_{N_3} = 125$ Kcal)

S_{N_3} = Solvation energy of the azide radical

Q = Energy required to bring the separated particles $Fe^{2+}(aq)$ and N_3 (aq) into a configuration and internuclear distance identical with that of the ion pair $Fe^{3+}N_3^-$ and therefore represents repulsion energy.

The energy change involved in the process :

$$Fe^{3+}(aq) + N_3^-(aq) \rightarrow Fe^{2+}(aq) + N_3(aq)$$

is given by the terms $I_{Fe^{2+}} - E_{N_3} - S_{N_3^-} + S_{N_3}$

Quantitative thermodynamic and kinetic data about the azide complex are still wanting. Weiss (1947) has given that the sum of the electron affinity of the azide radical and the solvation energy of the azide ions as 125 Kcal. The origin of Q is readily understood on the basis of Franck — Condon principle. According to the latter principle optical transition and electron transfer take place when (a) the inter atomic distance and (b) configuration of the hydra-

tion shell are identical in $Fe^{3+}N^{-}{}_3$ as well as $Fe^{2+}N_3$. These conditions will put the hydration shell in $Fe^{2+}N_3$ in a non-equalibrium configuration and therefore Q actually represents repulsion energy arising out of the non-equalibrium conditions. Q has been found to be approximately of the order of 45 Kcal and does not seem to vary much for different anions that complex with ferric ion. The energy required for photo excitation and electron transfer for the ion pair might be 40 — 50 kcal in excess of the endothermicity of the reaction $Fe^{3+} + N_3^- \longrightarrow Fe^{2+} + N_3$.

Initiation of polymerization: If polymerization were to be initiated by the primary product $Fe^{2+}N_3$ then according to the possibility I (a) or I (b) quantum yield with regard to ferrous ion production must go on increasing till unity is reached. On the other hand if we consider the possibility 2 (a) or 2 (b) in which N_3 radical is assumed to be the initiator, then the quantum yield under the justifiable assumption that $k_i[M] \gg k_o[Fe^{2+}]$ will be represented by $k_s/(k_s + k_d)$ which is a constant quantity. It was found for azide initiator in the presence of methylmethacrylate, acrylonitrile as well as methacrylic acid that γ went on increasing as the concentration of the monomers increased and reached a constant maximum value of $\sim 0{\cdot}5$ at pH $1 - 1{\cdot}1$. Possibility 3 (a) is also rejected on the ground that the expression for γ does not indicate the attainment of a constant value even after making the assumption that $k_i[M] > k_o[Fe^{2+}]$. We will therefore be correct in concluding that N_3 radicals alone initiate polymerization. The expression which would fit in with the experimental observations would then be;

$$\frac{dFe^{2+}}{dt} = \frac{k_s k_\varepsilon I}{k_d + k_s} \left(\frac{k_i[M]}{k_i[M] + k_o[Fe^{2+}]} \right) \quad .. \quad (A)$$

According to this equation, dFe^{2+}/dt should linearly vary with $k\varepsilon$ for azide. This has been found experimentally.

Equation (A) can be rearranged to give (B) and (C) below:

$$1 \mid (d\,Fe^{2+} \mid dt) = \frac{k_d + k_s}{k_s k_\varepsilon I} \left(\frac{k_o[Fe^{2+}]}{k_i[M]} + 1 \right) \quad .. \quad (B)$$

$$\text{or } I = \frac{dFe^{2+}}{dt} \left(\frac{k_o[Fe^{2+}]}{k_i[M]} \frac{k_d + k_s}{k_s k_\varepsilon} + \frac{k_d + k_s}{k_s k_\varepsilon} \right) \quad .. \quad (C)$$

According to equation (B) a plot of $I/(d[Fe^{2+}]/dt)$ against $[Fe^{2+}]$ or I/[M] should linearly vary. $[Fe^{2+}]$ in this expression was called mean Ferrous and was defined by Evans et. al (1951) as the sum of ferrous initially present plus half the ferrous ion produced during the time interval for the experiment. Such a definition is perhaps accurate when ferrous produced during the reaction is slightly higher than the ferrous ion initially added so that $d[Fe^{2+}]/dt$ would decrease as the mean ferrous increases. This was found to be the case for $Fe^{3+}OH^-$ and $Fe^{3+}Cl^-$. (Evans et. al. 1951). But in the case of $Fe^{3+}N^-_3$ initiator, ferrous ion produced during the reaction was so high in comparison with initially added ferrous that the computation of mean ferrous involved large errors. On the other hand linear variations of $I/(d[Fe^{2+}]/dt)$ with (I/[M]) with azide initiator for the three monomers tried, were achieved. From the slopes in these plots k_o/k_i were evaluated as 5×10^2 for acrylonitrite, 46 for methyl methacrylate and 50 for methacrylic acid. It has been found in case of $Fe^{3+}N_3^-$ that a plot of $d[Fe^{2+}]/dt$ against light intensity deviates at small light intensities under conditions of negligible scattering of light by the polymer. It is obvious from the expression (A) that perfect linearity is possible only if $k_i[M] > k_o[Fe^{2+}]$. If $k_o[Fe^{2+}]$ could not be neglected then the intensity plotted against $d[Fe^{2+}]/dt$ $[(k_o[Fe^{2+}]/k_i[M]) + I]$ must give linearity (C). This has been found to hold good for the azide complex (table 7).

From a comparison of the experimental results with the expressions for the rate of monomer disappearance under various possibilities it is possible to arrive at the possible terminating mechanism. On examination of the various expressions for dM/dt it is easily seen that if termination were to take place by free radicals by disproportionation, then dM/dt should be independent of light intensity and proportional to the second power of monomer concentration. On the other hand if termination takes place by mutual recombination, dM/dt will be proportional to square root of light intensity and proportional to 3/2 powers of monomer concentration if $Fe^{2+}N_3$ is the initiator or to first power monomer concentration if N_3 radical is the initiator. In case of $Fe^{3+}OH^-$ as well as $Fe^{3+}Cl^-$ it has been unequivocally proved (Evans et. al, 1951) that termination is one of combination OH or halide radical being the initiator but in case of $Fe^{3+}N^-_3$, in addition to the apriori evidence one could adduce, dM/dt being not independent of light intensity is also an indirect evidence for termination by combination for long chains.

In case of azide initiated methyl methacrylate polymers the chain length measured viscometrically was of the order of 800 to 1000 but the determination of nitrogen colorimetrically in the form of ammonia gave rather 12 — 14 atoms of nitrogen per polymers molecule. This high value of nitrogen is to be not relied upon especially in view of large uncertainty attached with colorimeter reading even for ammonia concentration of the order of 10^{-5}M. The sample of the polymer used would give a theoretical yield of ammonia concentration of the order of 10^{-6} M on the basis of two azide radicals per chain.

Ferric azide ion pair complex as an initiator might well be a special class of its kind distinct from $Fe^{3+}OH^-$ and $Fe^{3+}Cl^-$. From the high value of monomer disappearance by titration and low value of the weight of the polymer in azide initiated polymers one is tempted to conclude that the rate of termination is pretty high in these polymers resulting in short chains analogous to the chains initiated by Br or SCN radicals. Such short chains are also understandable on the basis of the low reactivity of the azide radicals having high resonance energy of stabilization. It is also quite possible that the azide radicals might break up due to bimolecular collisions to give nitrogen by one of the following processes :

$$N_3 + Fe^{3+}N_3^- \longrightarrow Fe^{2+} + 3N_2$$
$$N_3 + N_3 \longrightarrow 3N_2$$
$$N_3 + 2H_2O \longrightarrow N_2 + NH_2 + 2OH.$$

and OH radicals thus produced might initiate polymerisation. Also, the NH_2 radicals produced might lead to long chain polymers of length $\sim$ 1000 similar to chains obtained by the irradiation of hydrazine plus methylmethacrylate in which the primary photo chemical process is connected with photo dissociation of hydrazine to NH_2 radicals.

$$.. \quad N_2H_4 \xrightarrow{h\nu} NH_2 + NH_2.$$

With N_3 radicals produced primarily from $Fe^{3+}N_3^-$ it may be assumed that

(a) $2N_3 \longrightarrow 3N_2$ (occurs to a great extent).

(b) $N_3 + 2H_2O \longrightarrow 2OH + NH_2 + N_2$ (occurs to a small extent) Such assumptions are substantiated by the following observations :

(1) A large discrepancy in dM/dt between 'bromine titration' method and weight of the polymer; (2) High quantum yield with regard to ferrous ion; (3) Quantitative evolution of nitrogen in the absence of any monomer and low yield of nitrogen in the presence of the monomer.

Work on the lines indicated above is in progress in our laboratory and any definite conclusions to be drawn about the mechanism of the azide initiator will await further quantitative results.

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Influence of Some B Vitamins on the Conversion of Desthiobiotin into Biotin by *Neurospora crassa*

BY

M. O. Tirunarayanan and P. S. Sarma
(*Biochemical Laboratory, University of Madras, Madras-25*)

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ABSTRACT

Experiments indicate that the Ascomycete fungus, *Neurospora crassa*, is able to convert desthiobiotin into biotin using inorganic sulphur. Using antivitamins of folic acid, pyridoxin pantothenic acid. viz., 4-amino-pteroyl-glutamic acid (aminopterin), desoxypyridoxin hydrochloride and sodium ω-methyl-pantothenate, it has been found that none of these three vitamins are involved in the conversion of desthiobiotin into biotin in the mould. It is indicated that although these vitamins are not involved in the desthiobiotin → biotin conversion, the possibility of these being involved in the preliminary stages, such as synthesis of desthiobiotin or pimelic acid, cannot be excluded.

The importance of vitamins in cellular metabolism has been recognised for sometime past and is, perhaps, receiving increased attention to-day. The ability of certain micro-organisms to utilise precursors of vitamins or amino acids has in the main enabled biochemists to understand the processes involved in their formation. Considerable research work has established the relations existing among vitamins, vitamins with amino acids or purines or pyrimidines, and the role, vitamins play in tissue metabolism and function. It is also known that these vitamins function in a synergistic manner and a classical example of such a system may be found in the pyruvic oxidase of pigeon breast muscle. Littlefield and Sanadi (1952) have shown that this system necessarily depends on three vitamins,—thiamin, pantothenic acid and nicotinic acid,—functioning as co-factors for its activity. It is also known that one vitamin influences the biosynthesis or utilisation of another, and we had previously established a relation between biotin and nicotinic acid (Shanmuga Sundaram, Tirunarayanan and Sarma 1953), inositol and biotin (Tirunarayanan and Sarma (1953) and biotin and riboflavin (Tirunarayanan et al 1954). We had also established a relationship between folic acid and biotin in *Aspergillus oryzae* (Tirunarayanan and Sarma 1954). Shanmuga Sundaram, Ranganathan and Sarma (1951) reported that pyridoxin is able to in-

fluence the biosynthesis of nicotinic acid and vitamin C (ascorbic acid) in germinating pulses (*Phaseolus mungo*).

In the course of our studies on the biochemical functions of biotin, we were led to study the relationship of this vitamin with the other members of the vitamin B complex. We have been able to show that biotin is involved in the oxidative deamination of amino acids and fat formation in *Neurospora* (Sivasanker et al 1952), in the biosynthesis of inositol (Tirunarayanan and Sarma 1953), nicotinic acid and riboflavin (Shanmuga Sundaram et al 1953, Tirunarayanan et al 1954). Experiments have been carried out to elucidate whether the B vitamins have any influence on the biosynthesis of biotin, and the influence of folic acid, pyridoxin and pantothenic acid is reported in this study.

Experimental:

The organism, *Neurospora crassa*—8a (wild type), was grown on Fries' medium containing the following ingredients in grams per litre:

d (+) glucose	20
Ammonium tartarate	5
Ammonium nitrate	1
Pot. dihyd. phosphate	1
Sodium chloride	0·1
Magnesium sulphate	0·5
Calcium chloride	0·1
trace elements in mg. —	
Boron	0·01
Molybdenum	0·02
Iron	0·20
Copper	0·10
Manganese	0·02
Zinc	2·00
final reaction	pH 5·6

Biotin and desthiobiotin were added in quantities shown, after sterilisation, while the antivitamin compounds were added before sterilisation to the basal medium.

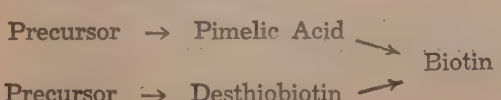
The media were dispensed in 10 ml. lots in 50 ml. conical flasks, sterilised at 15 lbs. pressure of steam for 20 min., and inoculated with a drop of a spore suspension obtained by suspending in saline washed spores from a 72-hour old slant of the same medium, and

adjusted to 80 percent transmission in a photo-electric colorimeter. The mycelia were harvested after an incubation period of 72 hours at room temperature (28-30° C.), washed thoroughly over a sintered glass funnel, pressed between folds of filter paper and dried to constant weight in a desiccator. The mycelia were weighed accurately using a Roller-Smith torsion balance.

Results and Discussion

The results of experiments carried out with a strain of *Neurospora crassa* indicate that this organism is able to utilise desthiobiotin for biotin synthesis, using inorganic sulphur, as reported by Tatum (1945). Figures I and II represent the growth response of the organism to biotin and desthiobiotin respectively. The effect of 4-amino-pteroyl-glutamic acid (aminopterin), sodium ω-methyl-pantothenate and desoxypyridoxin hydrochloride are represented by figures III, IV and V respectively.

Although the mechanism of synthesis of biotin in the cell has not been fully understood, it has been shown that pimelic acid and desthiobiotin are involved in the course of biotin synthesis. Du Vigneaud, Dittmer, Hague and Long (1942) observed, in the course of their investigation on the nutrition of *Corynebacterium diphtheriae,* that pimelic acid, shown to be an essential nutrient for this organism by Mueller and co-workers (1933), stimulated growth in the absence of biotin. They put forward that this compound may be utilised by the organism to form the n-valeric acid side chain of the biotin molecule. Eakin and Eakin (1942) further strengthened this suggestion by showing that biotin synthesis by *Aspergillus* is stimulated by introducing pimelic acid in the medium, and that this is further enhanced by cystine or cysteine which serve as source of organic sulphur. It was also observed by Tatum (1945) than an X-ray induced "biotinless" mutant of *Penicillium chrysogenum* (62078) was not able to convert desthiobiotin into biotin, although desthiobiotin accumulated in the culture. It had to be supplied with biotin for its growth. Tatum indicated, in view of these results, that the course of biotin synthesis is through desthiobiotin as an intermediate.



In a previous communication from this laboratory (Shanmugasundaram, Tirunarayanan & Sarma 1954), we had reported on the influence of biotin, using γ-3, 4- (ureylenecyclohexyl)-butyric

acid as the anti-biotin compound, on the utilisation of tryptophan for nicotinic acid synthesis by a "niacinless" mutant of *Neurospora crassa* (strain 39401). We had demonstrated that the anti-biotin compound preferentially inhibits the utilisation of tryptophan and that it does not in the least affect the utilisation of even the immediate degradation products of tryptophan. Thus, by a combination of mutant methodology and inhibition analysis, we had shown that such biochemical processes could be understood. In essentially the same way, we have tried the influence of folic acid, pantothenic acid and pyridoxin on the biosynthesis of biotin from desthiobiotin by a wild strain of *Neurospora crassa* which has biotin deficiency as a species characteristic and in which the genetic block lies at the precursor→desthiobiotin linkage.

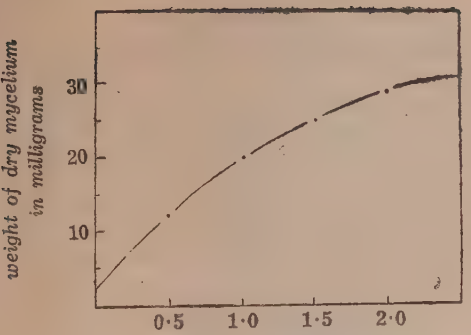
Effect of Folic Acid

Although there exists a remarkable relationship between folic acid and biotin, we have, however, not been able to detect whether biotin synthesis is affected by folic acid. It was shown by Sreenivasan (1952) that folic acid and biotin function in an antagonistic way with respect to nucleic acid synthesis by *Lactobacilli*, and that biotin in some manner suppressed the synthesis of nucleic acid catalysed by folic acid and vitamin B-12. It was also indicated that this depressing effect of biotin could be overcome by inositol. In previous communications (Tirunarayanan and Sarma 1954), we had indicated the nature of the antagonistic action of folic acid and biotin. It was shown that folic acid augmented the toxic effects of the insecticide, γ-hexachlorocyclohexane, in *Aspergillus oryzae* in inhibiting riboflavin synthesis and amylase production. While biotin was able to reverse the inhibition due to the insecticide, folic acid even prevented this influence of biotin. In the presence of folic acid, biotin was not able to overcome the inhibitory effects of γ-hexachlorocyclohexane.

In view of the above, it was thought that folic acid may in some manner be concerned with the biosynthesis or utilisation of biotin, and experiments carried out according to this suggestion, using 4-amino-pteroyl-glutamic acid (aminopterin) as the anti-folic acid compound, indicate that folic acid does not function in the conversion of desthiobiotin into biotin in *Neurospora*.

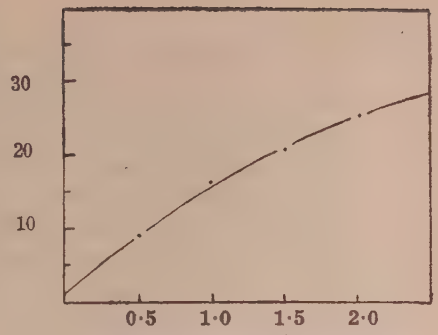
Effect of Pyridoxin

The conversion of desthiobiotin into biotin involves ring closure with the fixation of sulphur. This organism is able to utilise sul-



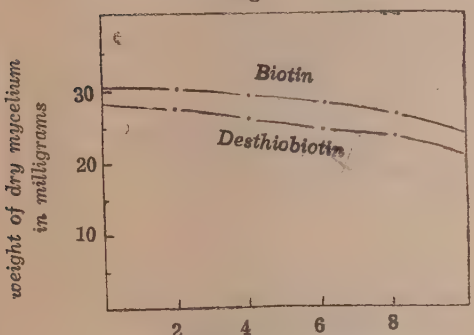
Biotin in millimicrograms per 10 ml. medium

Fig. I.



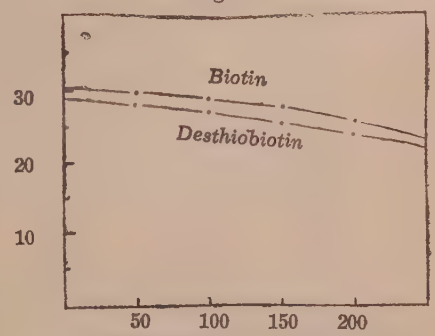
Desthiobiotin in millimicrograms per 10 ml. medium

Fig. II.



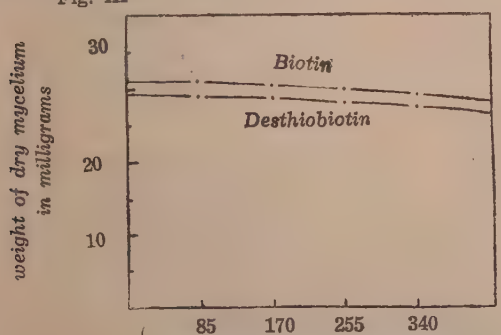
4-Amino-Pteroyl-Glutamic acid in micrograms per 10 ml. medium.

Fig. III



Desoxypyridoxin Hydrochloride in micrograms per 10 ml. medium

Fig. IV



Sodium-Methyl-Pantothenate in Micrograms per 10 ml. medium.

Fig. V

Fig. I. Growth response of *Neurospora crassa* to Biotin.

Fig. II. Growth response of *Neurospora crassa* to Desthiobiotin.

Fig. III. Influence of Aminopterin on the utilisation of Desthiobiotin and biotin by *Neurospora crassa.*

Fig. IV. Influence of Desoxypyridoxin HCl on the utilisation of Desthiobiotin and biotin by *Neurospora crassa.*

Figure V. Influence of Sodium-Methyl-Pantothenate on the utilisation of Desthiobiotin and biotin by *Neurospora crassa.*

phate sulphur for the synthesis. Pyridoxin is known to be involved in the fixation of sulphur (Binkley et al 1952). It was found that the enzymes responsible for the transfer of sulphur from homocysteine to the C-chain of serine to form cysteine were markedly activated by minute amounts of pyridoxal phosphate, and hence it was thought that pyridoxin may be involved likewise in the fixation of sulphur with desthiobiotin to form biotin. Moreover, pyridoxin and biotin appear to be rather closely related. Experiments carried out in this laboratory (Siva Sanker et al 1952) and elsewhere (Bender et al 1949, Burton (1951), Thayer and Horowitz 1952), indicate that biotin is involved in the formation of enzyme systems which are responsible for the deamination of serine and threonine and which in turn depend upon pyridoxal phosphate for their activity (Reissig 1952; Metzler and Snell 1952). Using desoxypyridoxin hydrochloride as the antagonist of pyridoxin we were able to find that pyridoxin also does not have any influence on the conversion of desthiobiotin into biotin by *Neurospora.*

Effect of Panthothenic Acid

In view of the close relationship existing between biotin and pantothenic acid (Dorfman et al 1942) in that a deficiency of either causes a decreased oxidation of pyruvate, it was thought that pantothenic acid may have some influence on the biosynthesis of biotin, but the experiments carried out in this direction using the sodium salt of ω-methyl-pantothenic acid as the anti-vitamin compound indicate, that the vitamin is not involved in the conversion of desthiobiotin into biotin.

The conversion of desthiobiotin into biotin must necessarily be an enzymatic reaction, in view of the fact that biochemical mutants have been produced, such as the strain of *Penicillium chrysogenum* (62078), lacking the ability to convert desthiobiotin. In conclusion, it may be mentioned that although these three vitamins do not have any specific function in the conversion of desthiobiotin into biotin in this mould, it is very likely that they may influence the synthesis of precursors of desthiobiotin or pimelic acid.

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Role of Biotin in Carbohydrate Metabolism of *Aspergillus oryzae*

BY

M. O. Tirunarayanan and P. S. Sarma
(Biochemical Laboratory, University of Madras, Madras 25)

ABSTRACT

Results of experiments carried out with a strain of *Aspergillus oryzae* by the technique of inhibition analysis, using γ-3, 4- (ureylenecyclohexyl) -butyric acid and biotin sulphone as the anti-biotin compounds, indicate that biotin has a pronounced influence on certain enzyme systems in the field of carbohydrate metabolism of the mould. It was observed that biotin is able to influence the oxidative dissimilation of pyruvate, succinate, lactate, malate and glucose in this organism. It is suggested that biotin may function in these systems not as a component or prosthetic group but only by influencing the synthesis of the whole or parts of the enzyme systems that are able to metabolise these compounds. It was observed that neither biotin sulphone nor the ureylene derivative had any influence on the amylase synthesised by this organism.

In a study on the biochemical functions of biotin, the influence of this vitamin on the various metabolic processes involved in the normal functioning of tissue has been investigated. In a previous communication from this laboratory (Siva Sanker, Tirunarayanan & Sarma, 1952) it was reported that biotin is involved in the oxidative deamination of amino acids in the Ascomycete fungus, *Neurospora*. We had also shown, for the first time, the influence of this vitamin in the probable biosynthesis and utilisation of inositol in the same mould (Tirunarayanan & Sarma, 1953). The role of biotin in the fixation of carbon dioxide with pyruvic acid to form oxalacetic acid in tissues have been proved beyond doubt. The first people to study this aspect of biotin influence were Lardy, Potter and Elvehjem (1947), who showed that oxalacetic acid could partially support the growth of *Lactobacillus arabinosus* in place of biotin and aspartic acid. Shive and Rogers (1947) indicated, by the technique of inhibition analysis, that the vitamin is involved in the synthesis of oxalacetic acid in *E. coli* and *L. arabinosus*. Very recently, Kaltenbach and Kalnitsky (1952) have reported that biotin is able to stimulate, within limited ranges, the enzymes capable of fixation

of carbon dioxide with pyruvic acid in both *E. coli* and *Proteus morganii.*

While the above reports dealt mainly with a function for biotin in carbon dioxide fixation, there have also been a considerable body of literature pertaining to the possible functions of biotin in the other fields of carbohydrate metabolism of the cell. It was suggested by Summerson, Lee and Partridge (1944) that biotin may be concerned with the oxidation of pyruvic and lactic acids. Ventricle slices from biotin-deficient ducks were found by Olson et. al. (1948) to decarboxylate succinate at a much lower rate than those obtained from biotin-fed normal ducks. It was also indicated that bacterial succinic dehydrogenase is appreciably reduced during biotin deficiency, and that this lost activity could in a large measure be restored by biotin (Ajl, Hart & Werkman 1950). Malate decarboxylation was also found by Lichstein and Umbreit (1947) to be influenced by biotin.

Consideration of the above reports led us to investigate the mechanisms and site of action of biotin in the various enzyme systems in the field of carbohydrate metabolism. We have been able to establish that some of the enzyme systems belonging to the tricarboxyic acid cycle of Krebs are considerably influenced by biotin.

Experimental.

Aspergillus oryzae, obtained from the National Collection of Type Cultures, National Chemical Laboratory, Poona, was carried by monthly subcultures on malt agar. For the experiment, the organism was grown on a modified Czapek-Dox medium containing the following in grams per litre:

d (+) glucose - 20;
potass. monohyd. phos. - I;
sodium nitrate - 3;
magnesium sulphate - 0·5;
potass chloride - 0·5;
trace elements in mg. per litre:-
molybdenum - 0·04; iron - 0·4; copper - 0·2;
boron - 0·02; manganese - 0·04; zinc - 4·0.
pH adjusted to 5·6.

The media were dispensed in 50 ml. lots in 250 ml. Erlenmeyer flasks, sterilised at 15 lbs. pressure for 17 minutes, and incubation was carried out, after inoculation with spores from a 7 day-old slant of the medium, for a period of ten days at 28-30°C.

This organism is able to synthesise biotin and as such does not depend on the presence of the vitamin in the medium for its growth. In order to diminish the synthesis or utilisation of the vitamin, we have used two compounds that have previously been established to exert pronounced anti-biotin activity; biotin suphone is perhaps the most potent among the anti-biotin compounds so far known (Dittmer, du Vigneaud, Gyorgy & Rose 1944) and has been shown to possess an anti-bacterial index of 280 against *L. casei* (Dittmer & du Vigneaud 1944). γ-3, 4- (ureylenecyclohexyl) -butyric acid has been found to have the maximum anti-biotin activity among benzene and cyclohexane derivatives of biotin (English et al 1945), and has been shown to interfere with biotin metabolism, such as synthesis of aspartic and oleic acids (Shive 1953).

The fully grown mycelia at the end of the incubation period were filtered through sintered glass funnels, washed thoroughly with cold distilled water, pressed between folds of filter paper and stored at 0° C. until use, although the time of storing did not exceed even six hours in any case. It was, however, found that prolonged periods of storage tended to diminish the activity of the enzymes studied. The tissues were separately ground in a waring blendor using glass-distilled water cooled to below 5°C. An aliquot of this suspension was taken for determination of total solids and the remaining used for enzyme assay.

Conventional Warburg techniques were employed in the determination of enzyme activity wherein oxygen was consumed, and the procedure outlined by Umbreit, Burris and Stauffer (1949) was strictly adhered to. Oxygen was used as the gas phase. 3 mg. of the various substrates were tipped from the side arm after equilibration, and the amount of oxygen consumed noted after a 20-minute interval. The pH conditions varied with individual substrates and are indicated in the respective figures. M/5 phosphate buffer was used throughout this investigation. Amylase activity was determined by the procedure outlined by Somogyi (1952) by a measurement of the reducing sugar formed (glucose equivalent) at the end of one hour at 37°C. from starch solution at a pH of 5·6. The results represented in terms of "amylase units" is indicative of the number in milligrams of reducing sugar formed by one gram mycelium at 37°C. in one hour from starch solution.

Results and Discussion.

The results of experiments carried out with a strain of *Aspergillus oryzae* by the technique of inhibition analysis are presented

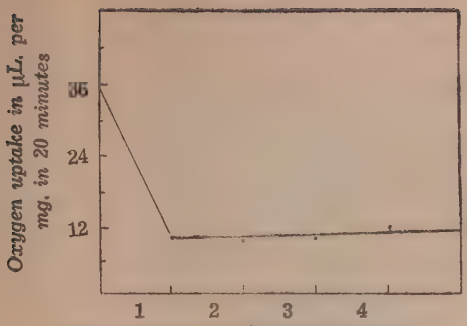
in the various tables and figures. Figures I to V indicate the influence of γ-3, 4-(ureylenecyclohexyl)-butyric acid on the oxidative dissimilation of pyruvate, succinate, lactate, malate and glucose respectively. Table I indicates the influence of biotin on the inhibition of the various enzyme systems by the ureylene compound. Tables II and III show the effect of both the ureylene compound and biotin sulphone on the amylase of this organism.

Pyruvic dehydrogenase has not so far been isolated in the pure state to be assured that it is a single protein, although a carboxylase involving pyruvic acid has been demonstrated in animal tissues. Lipmann (1939) has clearly indicated that the oxidation of pyruvic acid is a dehydrogenation of a postulated pyruvic phosphate followed by carbon dioxide elimination with the formation of acetyl phosphate, rather than a decarboxylation followed by oxidation (oxidative decarboxylation).

$$\text{pyruvic acid} = \text{acetyl phosphate} + CO_2$$

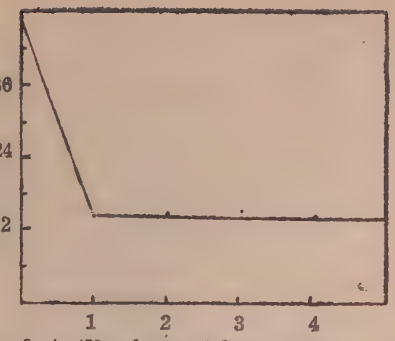
Although the role of diphosphothiamin in the principal pathways of pyruvate metabolism has been well established, it has been indicated that both pantothenic acid and biotin are also involved, (Stotz 1945, Dorfman et al 1942, Pilgrim et al 1942), but at what stage or through what mechanism, they were not able to account for. In the present investigation, it has been shown that biotin influences the oxidative dissimilation of pyruvate, and that the ureylene compound inhibits the oxidation of pyruvate (Figure I).

Recently, Littlefield and Sanadi (1952) worked out the mechanism of pyruvate oxidation by pigeon breast muscle. They showed that a minimum of four co-factors, besides the protein, are necessary for the oxidation of pyruvate, viz. diphosphothiamin, coenzyme A, DPN (diphosphopyridine nucleotide) and magnesium ion. There has not hitherto been any observation relating to possible influence of biotin in pyruvate oxidation, except in a general sort of way. In the course of an investigation on the influence of biotin on nicotinic acid synthesis from tryptophan in *Neurospora* and germinating pulses (*Phaseolus mungo*), we found that biotin was able to exert a pronounced influence on the synthesis of nicotinic acid (Shanmuga Sundaram et al 1953), and since DPN is one of the co-factors necessary for pyruvate oxidation, it is likely that decreased oxidation may be due to a decrease in the level of DPN. Further, it has been observed in *Neurospora* (Nason et al 1951) that there is a marked accumula-



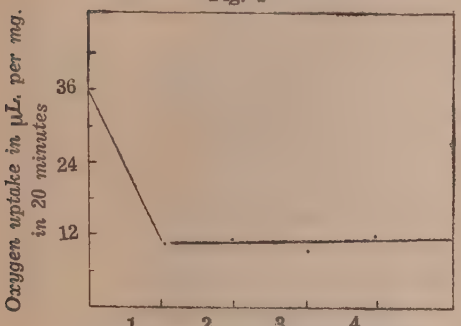
γ-3, 4- (*Ureylenecyclohexyl*) -*Butyric acid in milligrams per 25 ml.*

Fig. I



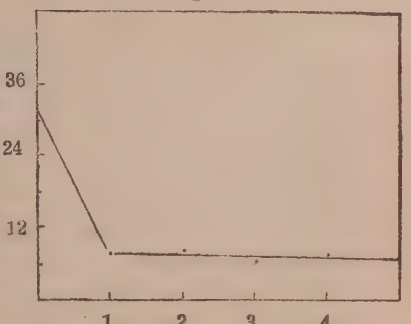
γ-3, 4- (*Ureylenecyclohexyl*) -*Butyric acid in milligrams per 25 ml.*

Fig. II.



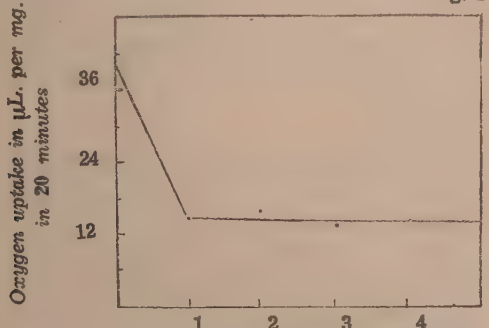
γ-3, 4- (*Ureylenecyclohexyl*) -*Butyric acid in milligrams per 25 ml.*

Fig. III.



γ-3, 4- (*Ureylenecyclohexyl*) -*Butyric acid in milligrams per 25 ml.*

Fig. IV.



γ-3, 4- (*Ureylenecyclohexyl*) -*Butyric acid in milligrams per 25 ml.*

Fig. V.

Fig. I. Influence of γ-3, 4- (Ureylenecyclohexyl) -Butyric acid on Pyruvate Oxidation by Aspergillus Oryzae.

Fig. II. Influence of γ-3, 4- (Ureylenecyclohexyl) -Butyric acid on Succinate Oxidation by Aspergillus Oryzae.

Fig. III. Influence of γ-3, 4- (Ureylenecyclohexyl) -Butyric acid on Lactate Oxidation by Aspergillus Oryzae.

Fig. IV. Influence of γ-3, 4- (Ureylenecyclohexyl) -Butyric acid on Malate Oxidation by Aspergillus Oryzae.

Fig. V. Influence of γ-3, 4- (Ureylenecyclohexyl) -Butyric acid on Glucose Oxidation by Aspergillus Oryzae.

tion of DPNase during biotin deficiency, and that this enzyme, unlike mammalian enzymes which catalyse the breakdown of DPN into nicotinamide mononucleotide and adenylic acid, breaks off DPN at the nicotinamide-ribose linkage. This increase in DPNase activity has been found to be suppressed by addition of biotin. Hence, the role biotin is likely to play in pyruvate oxidation is indirect, by controlling the biosynthesis of one or more co-factors like DPN, although its influence on the protein part of the system cannot altogether be excluded.

Succinic Dehydrogenase catalyses the breakdown of succinate to fumarate, and the role cytochromes play in succinate oxidation has been well recognised. Although the mechanism of action is yet not clear as to the source from which hydrogen is transferred to fumaric acid to form succinic acid, there are reports in literature to indicate that in the series of oxidative steps involving succinic acid, pyridine nucleotides are also involved. In the course of an experiment on the enzymatic breakdown of d (+) biotin by kidney cortex, Baxter and Quastel (1953) reported that the system metabolising biotin is inhibited by malonate. It was suggested that since malonate happens to be well known to have an influence on succinate metabolism, the inhibition by malonate of the system metabolising biotin may be due to a function of the latter in the metabolism of succinate and related enzymes of the tricarboxylic acid cycle. Only further work would reveal the mode of action of biotin in this system.

Lactic and Malic Dehydrogenases. These two enzymes depending on either DPN or TPN for their activity have been shown to catalyse the oxidation of lactic and malic acids respectively. It has been indicated that pigeon liver contains a TPN-dependent malic dehydrogenase, and the mechanism that comes into play depends to a large extent on the source of the enzyme itself (Salles and Ochoa, 1950). The role that biotin and nicotinic acid play in malate dissimilation has been well indicated (Blanchard et al, 1950). It was shown that biotin is not involved in it as a prosthetic group or even a component of such a group, since addition of biotin did not increase the activity of the cells deficient in biotin, while nicotinic acid was able to rapidly restore the lost activity of the cell to metabolise malate. Hence, it is likely that biotin may not function in these systems, oxidation of malate and lactate, as a prosthetic group, but that its function is likely through an interference in the biosynthesis of nicotinic acid and DPN.

Glucose Dehydrogenase and Glucose Oxidase. The enzymes capable of oxidising glucose have been found to operate with either a pyridine nucleotide or a flavin, depending upon the source of the enzyme itself. Early observations have indicated that biotin has a pronounced influence on the fermentation of glucose (Winzler et al, 1944; Srinivasaya and de Souza, 1945), and experiments carried out using the ureylene compound indicate that biotin is involved in the oxidation of glucose in *Aspergillus oryzae* (Figure V). In view of our observation that biotin is concerned with the biosynthesis of riboflavin and nicotinic acid (Shanmuga Sundaram et al, 1953), it is very likely that interference by biotin in this field is primarily through a restriction of the availability of the co-factors necessary for the oxidation of glucose. At the present moment, however, we are unable to indicate as to whether biotin is involved in the synthesis of the protein part of all these enzyme systems, and experiments are under way to elucidate this aspect of the problem.

Amylase. In the course of an investigation on the influence of biotin on the inositol-γ-hexachlorocyclohexane relationship in this mould (Tirunarayanan and Sarma, 1954) we observed that while the gamma isomer inhibited the synthesis of the enzyme, biotin was able to overcome the inhibitory effect. This mould is known to synthesise only the α-amylase, which converts starch to glucose and iso-maltose. It has been found that the pH optima is between 5·2 and 5·6. It was thought desirable to study if biotin by itself has any influence on the synthesis of amylase by this mould. Accordingly, experiments were carried out using both γ-3. 4- (ureylenecyclohexyl) -butyric acid and biotin sulphone as the anti-biotin compounds, and the results, presented in Tables II and III, indicate that biotin does not have any influence on the amylase in this organism.

In conclusion, it may be mentioned that the principal pathways of biotin function in the oxidative dissimilation of pyruvate, lactate, malate, glucose and succinate may, in the main, be due to an influence on the synthesis of either DPN or FAD, that serve as co-factors in these systems, although the possibility that biotin may have some influence on the synthesis of the protein moiety cannot be excluded.

TABLE I

Influence of γ-3, 4-(Ureylenecyclohexyl)-Butyric Acid and Biotin on the Dehydrogenases of *Aspergillus oryzae*

Supplement to basal medium per 50 ml.	Oxygen uptake in µl. per mg. in 20 min.				
	Succinate	Pyruvate	Lactate	Glucose	Malate
Basal Medium (BM) (control) ..	47·0	36·6	43·5	40·5	32·0
BM+ureylene compound Img.) ..	12·8	10·2	9·4	14·6	8·5
BM+ureylene compound (Img.) ..	32·6	22·3	27·8	27·2	20·4
+biotin (25 γ) ..					

TABLE II

Influence of γ-3, 4-(Ureylenecyclohexyl)-Butyric Acid on the Amylase of *Aspergillus oryzae*

ureylene compound mg./50 ml.	Amylase units
0	2400
1	2200
2	2245
3	2360
4	2320
5	2290

TABLE III

Influence of Biotin Sulphone on the Amylase of *Aspergillus oryzae*

biotin sulphone μg./50 ml.	Amylase units
0	2450
1	2380
2	2410
3	2280
4	2300
5	2360

Acknowledgements

The authors wish to express their gratitude to Dr. Richard O. Roblin, Jr., American Cyanamid Company, for the generous gift of γ-3, 4-(ureylenecyclohexyl)-butyric acid, and to Dr. Vincent du Vigneaud, Cornell University Medical College, for biotin sulphone used in this investigation. The work reported herein forms part of the thesis submitted by one of us (MOT) to the University of Madras for the degree of Master of Science.

Foot-note to Text Figures

Figure I. γ-3, 4- (ureylenecyclohexyl) -butyric acid inhibition of pyruvate oxidation by *Aspegillus oryzae.*

3 mg. pyruvate in I ml.; enzyme suspension—2 ml.; 0·2M phosphate buffer—3 ml.; pH 7·0; 37° C.

Figure II. γ-3, 4- (ureylenecyclohexyl) -butyric acid inhibition of succinate oxidation by *Aspergillus oryzae.*

3 mg. succinate in 1 ml.; enzyme suspension—2 ml.; 0·2M phosphate buffer—3 ml.; pH 7·2; 37° C.

Figure III. γ-3, 4- (ureylenecyclohexyl) -butyric acid inhibition of lactate oxidation by *Aspergillus oryzae.*

3 mg. lactate in 1 ml.; enzyme suspension—2 ml.; 0.2M phosphate buffer—3 ml.; pH 7·4; 37° C.

Figure IV. γ-3, 4- (ureylenecyclohexyl) butyric-acid inhibition of malate oxidation by *Aspergillus oryzae.*

3 mg. malate in 1 ml.; enzyme suspension—2 ml.; 0.2M phosphate buffer—3 ml.; pH 7·4; 37° C.

Figure V. γ-3,4- (ureylenecyclohexyl) -butyric acid inhibition of glucose oxidation by *Aspergillus oryzae.*

3 m. glucose in 1 ml.; enzyme suspension—2 ml.; 0.2M phosphate buffer—3 ml.; pH 5·6; 37° C.

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Soil Conditions and Root Diseases XI. *Neocosmospora vasinfecta* Smith Disease of *Cajanus cajan*

BY

(Mrs.) T. S. Sarojini,

University Botany Laboratory, Madras-5

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ABSTRACT

An ascogenous fungus identified as *Neocosmospora vasinfecta* Smith, was isolated from roots of wilted *Cajanus* plants in the laboratory experimental plot. The strains evolved from the asexual spore forms of the ascogenous fungus were more pathogenic than the parent strain and *F. udum,* the established wilt pathogen of *Cajanus.* It is suggested that *N. vasinfecta* Smith be classed with the 'soil inhabitant' class of facultative saprophytes like many members of the *Fusarium,* since it has been found to occur in many arable and scrub jungle soils examined in this laboratory over many years.

The genus *Neocosmospora* with one species *N. vasinfecta* Sm. was established by Smith (1899) for a fungus causing wilt of cotton, watermelon and cowpea in the United States of America. Cross inoculation trials were not successful except with watermelon and therefore the parasitism of the fungus could not be fully established. The only evidence brought forward was that the conidial stages of *Neocosmospora* resembled closely the micro- and macro-conidial forms of *Fusarium.* Following Smith's discovery, this fungus was recorded on cotton and other hosts by Delacroix (1902-3), Jaczewski (1903), Zimmerman (1904), Van Hall (1905), and Malkoff (1906); but in all these investigations, identification of the causal pathogen was made from conidial stages alone and perithecia were not found. *N. vasinfecta* was believed by many earlier workers on wilt diseases (Smith, 1899; Orton, 1900; Fulton, 1907; Hibbard, 1910) to be the perfect stage of some wilt producing Fusaria, although no proof was presented to substantiate this belief. Zaprometoff (1925, 1926) attributed the cotton wilt disease to *N. vasinfecta* with its conidial stage *Fusarium vasinfectum,* but later (1927) revised his opinion and named the latter

as the causal pathogen as it was not observed to form perithecia. Recently the occurrence and parasitic activity of *N. vasinfecta* were conclusively investigated by Nisikado and Yamauti (1937, 1938) in connection with the seedling wilt of the silk cotton tree, *Albizzia julibrissin* Durraz, in Japan. The latest report on the occurrence of this fungus is by Moreau and Moreau (1950).

In India, Butler (1910) discovered and identified the perithecia occurring on roots of wilted red gram plants as belonging to *N. vasinfecta* Sm. after investigating fully the cultural and parasitic aspects of this fungus. But he found it irresistable to conclude after a series of failures to produce infection in red gram plants that *N. vasinfecta* was a common soil saprophyte developing its perfect form on roots of several crop plants and was wholly unconnected with the wilt diseases of the particular hosts, red gram, cotton, sesame and indigo, investigated so far in India. Later, red gram and sann hemp wilt in India were said to be caused not only by *Fusarium udum* but also to a lesser degree by *N. vasinfecta* (Mitra, 1934). A high percentage of wilt was, however, obtained by him in pot experiments with *N. vasinfecta* on sann hemp.

In August 1948, this fungus was found on roots of wilted red gram plants in the laboratory garden plot. The cultural characters and general behaviour of this isolate agreed very closely with the descriptions furnished by Butler, who found his strain to be indistinguishable from *N. vasinfecta* Sm. The author failed, however, to substantiate Butler's finding of its being incapable of parasitism. At this juncture, it was felt very necessary to determine conclusively the virulence of the fungus on red gram, as evidence that it could no longer be regarded as a pure saprophyte had already been brought forth by Nisikado and Yamauti, and Mitra.

Material and Methods

The general technique followed as regards pathogenicity, recording of wilt index and re-isolation of the organism was as described earlier by the author (1951). The strains tested in the pathogenicity trials were derived from single conidial (non-septate and septate), chlamydospore and ascospore cultures obtained from the ascogenous fungus originally isolated in 1948. The strains so derived from asexual spores differed from the mother culture in that the production of perithecia was considerably low accompanied by a profuse growth of aerial mycelium, thus resembling a normal

'Fusarium' culture. The pathogenicity of these strains was investigated with a view to find out their relative parasitic capabilities on *Cajanus* as compared with the established wilt fungus *Fusarium udum*.

Experimental

The results presented in Table I show that all the strains were pathogenic on red gram to a greater or lesser extent. thus confirming the results obtained in the original infectivity test conducted in 1948. Total emergence of seeds was complete seven days after sowing. Wilting started on the seventh day approximately and continued for a week, the infection percentage increasing up to 100 per cent in one series. In the *F. udum* and ascospore series of *N. vasinfecta*, the rate of incidence was lower and comparatively slow. Disease symptoms manifested in all the series were almost similar to that obtained with *F. udum*. If seedlings were infected at the first leaf stage, a definite indication of this was the preliminary curling of the tips of leaves. In older seedlings, a gradual yellowing of the leaflets was the first symptom followed by fairly rapid wilting and collapse of the plant. At this stage microscopic examination of the discoloured and diseased portions of the hypocotyl and roots of plants infected with the ascogenous strain revealed numerous perithecia, while the other series yielded the asexual spore forms in enormous numbers.

It was interesting to note that highly significant results were obtained on statistical analyses of the experimental data. The series infected with the asexual spore derivatives behaved similarly as regards pathogenicity while the wilt percentage obtained by the ascogenous fungus and *F. udum* were similar and significant. The conidial strains of *N. vasinfecta* were more pathogenic than the ascogenous strains and *F. udum*. Smith (1899) also found that the cultures derived from both micro- and macro-conidia of *N. vasinfecta* were virulent.

Discussion

The pathogenicity of *N. vasinfecta* to water-melon, cotton and other plants has been generally disputed since the report of Butler (1910) and Higgins (1911) on the saprophytic nature of the fungus. Although Butler also obtained some infection on *Cajanus*, he considered that these apparent infections could be accounted for by

accidental inoculation from some other source, as *Cajanus* wilt was highly prevalent in that area. The sources of external infection in that case would be too numerous to exclude. Further, he stressed the non-pathogenic nature of the fungus to such an extent as to even doubt the origin of the cultures derived by Smith (1899), who initially claimed that *N. vasinfecta* was responsible for cotton wilt.

Nisikado and Yamauti (1937, 1938) were the first to bring forth conclusive evidence that *N. vasinfecta* could no longer be regarded as a pure saprophyte. This fact has been further strengthened by the present study, where the ascogenous strain of *N. vasinfecta* was found to be as pathogenic as *F. udum,* while the asexually derived strains were distinctly more virulent than either of these. It is of considerable interest to note here the concluding remarks of Smith, who, although was able to establish fully the parasitism of the water-melon isolate only, "had no doubts whatever as to the parasiitc nature of the cotton or cowpea isolate, or as to the genetic relationship of the various spore forms on cotton and of the perithecia to the conidial stages on the water-melon, but that these points had not been definitely proved or settled by satisfactory infection experiments and by deriving one spore form from the other in pure culture". This is precisely what has been taken up for investigation in the present paper.

The strain of *N. vasinfecta* isolated by the author was seen to conform morphologically with Butler's isolate (1910) in almost all respects, except that its definitely parasitic character established in this study is opposed to the findings of Butler and Wollenweber and Reinking (Wollenweber, 1913; Wollenweber and Reinking, 1935) who regarded this fungus as wholly unconnected with *Cajanus* wilt and was but a mere soil saprophyte developing on rotting roots. This work is, therefore, in greater agreement with the results obtained by Mitra (1934) and Nisikado and Yamauti (1937, 1938).

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Table I showing the analysis of variance in pathogenicity tests conducted on *Cajanus* with *F. udum* (conidiospore derivative) and strains of *N. vasinfecta* (conidiospore and ascospore derivatives).

No.	Strains	Total wilt-Mean (%)
1.	*Fusarium udum* ..	44
2.	*N. vasinfecta*	
	(a) ascospore derivative ..	63
	(b) chlamydospore derivative ..	83
	Conidiospore derivatives	
	(c) non-septate ..	82
	(d) septate ..	100
3.	Control (healthy) ..	0
	Standard Error $= \sqrt{43} = 10{\cdot}3$	
	Critical difference $= 30{\cdot}6$	
	2d 2b 2c 2a 1 3.	

* Conidiospores of *N. vasinfecta* are designated 'non-septate' and 'septate' in this investigation mainly to avoid any controversy at this stage particularly in view of divided opinion in literature on whether they are to be classed as micro- or macro-conidia or not. However, further work on the fungus may indicate adherence to one view or another.

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